UNIVERSITY OF GLASGOW
(Department of Chemistry)

The Application of Irreversible Thermodynamics to Transport Processes in Concentrated Binary Electrolyte Solutions.

A Thesis Presented for the Degree of Ph.D. by
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ERRATA

Page 6	In equation (2.5), read '> 0', not '$\geqslant 0$'.
Page 7	In equation (2.6), read '$dS_{int}/dt = \ldots\ldots\ldots$'
Page 36, line 6	The reference number above Pikal should be 141.
Page 70	The pairs of columns in Table (4.17) should be headed in turn, from left to right, LiCl, NaCl, KCl, RbCl, CsCl.
Page 102	The silver-silver iodide electrodes were prepared by an electrolytic-electrolytic technique.
Page 115	In Figure 6.1, the units of D are cm^2/sec. Concentration is expressed in molar units.
Page 121	In Table (6.5), the units of equivalent conductivity are $(ohm\ cm)^{-1}$.
Page 146	Data for the density equations were obtained from reference 18.

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ABSTRACT

Transport processes in isothermal binary electrolyte solutions have been studied by means of an irreversible thermodynamic approach.

Relationships between the experimentally accessible quantities of transport number, diffusion coefficient, and conductivity are presented in terms of the phenomenological coefficients L_{ij} and R_{ij}.

The isotopic diffusion coefficients of chloride ion in rubidium and caesium chloride, caesium ion in caesium chloride, and of tritium-labelled water in lithium, sodium, potassium, rubidium, and caesium chloride solutions have been measured in the concentration range 0-2.5M. These have been combined with existing literature data in order to obtain the phenomenological coefficients representing isotope-isotope friction.

The variations with concentration and relative magnitudes of these quantities have been discussed in terms of water structure and ionic environment.

Equivalent conductances, transport numbers, and diffusion coefficients have been measured for solutions of cadmium iodide in the concentration range 0-1.0M. These data have been combined with activity and density data from literature sources and the phenomenological coefficients L_{ij} and R_{ij} obtained.

The variation of these quantities with concentration has been discussed and interpreted in terms of the formation of complex species in the cadmium iodide system.

Nomenclature

A	Total effective cross-section of diaphragm pores. (cm^2).
A_i	Affinity of chemical reaction. (joules/mole).
a_i	Activity of species i.
c_i	Concentration of species i. (moles/litre).
C_p	Capacitance. (farads).
D, D_v	Volume-fixed differential diffusion coefficient. (cm^2/sec.).
$\overline{D}$	Integral diffusion coefficient. (cm^2/sec.).
$\overline{D}(t)$	Concentration-averaged diffusion coefficient. (cm^2/sec.).
D_0	Solvent-fixed diffusion coefficient. (cm^2/sec.).
D_{ii}	Diffusion coefficient of ionic species i. (cm^2/sec.).
D^o	Diffusion coefficient at infinite dilution. (cm^2/sec.).
d	Distance. (cm.).
dS	Total entropy change. (e.u.).
dS_e	Entropy change due to interactions with the exterior.(e.u.).
dS_{int}	Internal production of entropy. (e.u.).
E	Electro-motive force. (volts).
F	Faraday of electricity. (coulombs/equivalent).
f	Mean molal activity coefficient.
I	Current density. (amps/cm^2).
J_{ch}	Flow of chemical reaction.
J_i	Flow of species i. (moles/cm^2sec.).
J_s	Flow of entropy. (Chapter 2.2).
	Solvent-fixed flow of electrolyte, (Chapter 2.7.4), in moles/cm^2sec.
$J(t)$	Flux of solute at time t. (moles/cm^2sec.).
k	Specific conductivity. (ohm cm.)$^{-1}$
L	Thermodynamic diffusion coefficient. (moles^2/joule.sec.cm.).
L_{ii}	Intrinsic mobility of species i. (moles^2/joule.sec.cm.).
L_{ij}	Cross-coefficient of mobility. (moles^2/joule.sec.cm.).
l	Diffusion path length. (cm.).
M	Molarity. (moles/litre).
M_i	Molecular weight of species i.
m_i	Molality of species i. (moles/Kg.).
N	Normality. (equivalents/litre).
R	Gas constant. (joules/mole.degree).
R_p	Apparent resistance. (ohms).

R_{ij}, R_{i0}	Coefficient of friction between species i and j, and between species i and solvent, respectively. (joule.sec.cm./moles^2).
R_t	True resistance. (ohms).
r	Thickness of medium. (cm.).
T	Absolute temperature. (°K).
T_i	Integral transport number of species i.
t	Time. (secs.).
t_i^c	E.m.f. transport number.
t_i^h	Hittorf transport number.
V	Volume. (cm.^{3}).
v_i	Velocity of species i. (cm./sec.).
X_i	Thermodynamic force on species i. (joules/mole.cm.).
x	Distance. (cm.).
y	Mean molar activity coefficient.
z_i	Signed valency of species i.
α	Function defined by equation (2.30).
β	Cell constant.
ζ	Viscosity. (poise).
ζ_0	Viscosity of solvent. (poise).
Λ	Equivalent conductivity. (cm.^{2}/ohm.equivalent).
λ_i^0	Limiting equivalent conductivity of species i. (cm.^{2}/ohm.equivalent).
μ_i	Chemical potential of species i. (joules/mole).
μ	Refractive index.
$\tilde{\mu}_i$	Electrochemical potential of species i. (joules/mole).
μ_{ij}	Chemical potential of neutral electrolyte. (joules/mole).
γ_i	Stoichiometric ionisation coefficient of ion i.
γ	Sum of stoichiometric ionisation coefficients.
σ	Rate of entropy production.
τ	Prediffusion time. (secs.).
ψ	Electrical potential. (volts).
Φ	Dissipation function. (energy/unit time).
ω	Angular frequency. (Hertz).

CHAPTER 1

INTRODUCTION

INTRODUCTION

Classical theories of the behaviour of electrolyte solutions under the influence of concentration or electrical potential gradients are based on the laws of interionic attraction and the concept of ion atmosphere. As a result, these theories successfully account for the observed transport properties in very dilute solutions.

In such solutions, long-range coulombic forces are the principal interaction, and classical theories of conductance and diffusion are based upon the assumption that the kinetic friction between an ion and the bulk solvent, which determines λ_i° for example, remains unaltered when a finite concentration of solute is present. It is further assumed that any additional friction between ions and solvent may be ascribed to distortion of the ion atmosphere due to the electrophoretic and relaxation effects.

Classical theories do not, however, take into account specific effects, such as ion association and complex formation in solution, variation in the structure of the bulk solvent, changes in solvation around the ion, and local variations in viscosity and dielectric in concentrated solutions.

As a consequence, classical theories fail in solutions more concentrated than approximately 0.001N for completely dissociated 1:1 electrolytes, with lower limits for unsymmetrical electrolytes.

Various attempts have been made to extend the concentration range of classical equations by taking into account short-range interionic effects. The conductance theories of Pitts and of Fuoss and coworkers have succeeded in extending the limit of validity to approximately 0.05N for completely dissociated 1:1 electrolytes. In the case of more complex solutions, such as associated electrolytes, this limit is reduced to approximately 0.025N.

Within the last few decades, however, an alternative approach to the problem has been developed. The basis of this approach is the phenomenon of coupling between forces and flows in a transport experiment. Considering cond-

uctance, in which cations and anions flow simultaneously in opposite directions under a gradient of electrical potential, the flow of the cation is influenced by the force on the anion, and vice-versa. The phenomenon of coupling was recognised as long ago as 1854 by Lord Kelvin, in a study of the thermoelectric effect, but the first rigorous mathematical treatment was given by Onsager[130], in 1931. Further expansion and generalisation of Onsager's theory of irreversible thermodynamics is described in a number of treatises.[48,76,144]

The application of irreversible thermodynamics to isothermal transport processes in electrolyte solutions is due chiefly to Miller.[107-109] The theory of irreversible thermodynamics as presented by Miller may be directly applied to experimentally measurable transport properties, leading to a general description which is valid over any concentration range. Transport processes are described in terms of linear phenomenological coefficients which are a specific measure of ion-ion and ion-solvent interactions. The concentration dependence of the transport properties conductance, diffusion coefficient and transport number, are rationalised in terms of these phenomenological coefficients, which are clearly more fundamental than the transport processes themselves. Knowledge of the phenomenological coefficients as functions of concentration for a given system allows the complete characterisation of any vector transport process, no matter how complex, in that system.

The theory of irreversible thermodynamics is presented in Chapter 2, in which it is shown that, for a binary electrolyte solution, only three transport quantities, diffusion coefficient, D, conductance, Λ, and transport number, t_i, are required in order to derive the phenomenological coefficients, L_{ij} and R_{ij}. As previously stated, these L_{ij} and R_{ij} coefficients qualitatively interpret the concentration dependence of the transport processes. A more meaningful interpretation is obtained when a series of electrolytes, such as the alkali metal chlorides, is

considered. Sufficient data is available[29,67,109] for the phenomenological coefficients to be calculated for this series over the concentration range 0-3.0M. However, comparable data for isotopic diffusion coefficients of component ions and water are incomplete. In particular, diffusion data for chloride ion in RbCl and CsCl, for rubidium ion in RbCl, for caesium ion in CsCl, and for water in LiCl,NaCl,KCl,RbCl,and CsCl, are lacking. These have been obtained in this study, using a diaphragm cell, for all but rubidium ion in RbCl.

It is shown that the two sets of data may be combined to yield Onsager frictional coefficients ($r_{ii'}$) or mobility coefficients ($l_{ii'}$) which measure the kinetic interaction between isotopes as a function of concentration for each salt solution. Since the $l_{ii'}$ contain frame of reference contributions with water solvent, their interpretation is difficult, but these may be compared with values calculated from the Onsager limiting law. Frictional coefficients are more explicit. The main factor contributing to the diffusion coefficient of ions, D_{ii}, remains ion-water friction, because interionic friction between oppositely charged ions is largely cancelled by isotope-isotope friction in the expression for D_{ii}. Water diffusion, D_{00}, is shown to be primarily due to isotope-isotope friction, between water and water, which is the sole contribution to D_{00} for pure water.

In a separate section of this thesis, measurement of the transport quantities t_i, D, and Λ, is described for the system cadmium iodide-water. Using these data, the irreversible thermodynamic parameters L_{ij} and R_{ij} are obtained and compared with similar data for a completely ionised 2:1 salt system, $CaCl_2$, and one in which self-complexing also occurs, $CdCl_2$. A semi-quantitative interpretation of the effects of self-complexing in the cadmium iodide is developed and discussed.

Curve-fit data and details of computer programmes used in this work are presented in two Appendixes.

CHAPTER 2

THEORY OF IRREVERSIBLE THERMODYNAMICS AS APPLIED TO TRANSPORT PROCESSES IN CONCENTRATED BINARY ELECTROLYTE SOLUTIONS.

2.1 Entropy Production: Systems undergoing irreversible processes may be divided into an infinite number of macroscopically small local subsystems.[107] Each subsystem may be considered to be in local equilibrium,[14,4] despite the gradients of thermodynamic parameters which give rise to the irreversibility.

This assumption is valid if perturbations from equilibrium are small, and permits the application of all the results of classical thermodynamics to a given subsystem.

The change of entropy in a subsystem during an irreversible process is given by:

$$dS = dS_e + dS_{int} \tag{2.1}$$

where dS_e is the change in entropy due to a reversible interaction with the exterior and dS_{int} is due to production of entropy within the system itself. dS_{int} is constrained by the inequality:

$$dS_{int} \geqq 0 \tag{2.2}$$

That is, dS_{int} is zero for a reversible change but positive when a change occurs irreversibly.

In an isolated system in which neither energy nor matter can be exchanged,

$$dS_e = 0 \tag{2.3}$$

and the total entropy production becomes

$$dS = dS_{int} \geqq 0 \tag{2.4}$$

If two such systems are enclosed to form an isolated system, and in each some irreversible process takes place, then

$$dS = dS^1_{int} + dS^2_{int} \geqq 0 \tag{2.5}$$

It is further postulated[137] that in every macroscopic region of the system the entropy production is positive.

$$\text{i.e.} \quad dS^1_{int} \geq 0 \quad \text{and} \quad dS^2_{int} \geq 0.$$

In the special case of coupled chemical reactions, however, the rate of entropy production , dS/dt , is given by

$$dS/dt = dS^1_{int}/dt + dS^2_{int}/dt \geq 0$$

and it is possible for dS^1_{int}/dt to be positive and dS^2_{int}/dt to be negative, providing their sum is positive. Thermodynamic coupling of this kind, such that a spontaneous chemical reaction drives another against its spontaneous tendency, is an essential feature of living systems.[137]

2.2 The rate of Entropy Production and the Dissipation Function:

The rate of entropy production in a system may be considered to be the sum of contributions from all volume elements, so that

$$dS_{int} = \int_V \sigma . dV \qquad (2.6)$$

where σ is the local rate of production of entropy per elemental volume, dV.

σ may be identified as a sum of terms, each being a product of a flux and a conjugate thermodynamic force. Thus the choice of flows and forces is to some extent arbitrary, provided the products have the dimensions of entropy production.

For a system in the steady state, σ is given by the relationship[76]

$$\sigma = (J_s/T)\,\text{grad}(-T) + \sum_{i=1}^{n} (J_i/T)\,\text{grad}(-\tilde{\mu}_i) + J_{ch}.(A_i/T) \qquad (2.7)$$

where J_s, J_i, and J_{ch} are the fluxes of entropy, matter, and chemical reaction. The conjugate forces are defined as the

negative gradients of temperature, T, electrochemical potential, $\tilde{\mu}_i$, and affinity, A_i.

σ may be replaced by the dissipation function, $T\sigma$, which is a measure of the rate of local dissipation of free energy, with dimensions of energy per unit time. Rearrangement of equation (2.7) gives

$$T\sigma = \Phi = J_s.\text{grad}(-T) + \sum_{i=1}^{n} J_i.\text{grad}(-\tilde{\mu}_i) + J_{ch}.A_i \qquad (2.8)$$

Considering only isothermal irreversible processes in electrolyte solutions in which no chemical reactions are occurring, the dissipation function reduces to:

$$\Phi = \sum_{i=1}^{n} J_i.\text{grad}(-\tilde{\mu}_i) \qquad (2.9)$$

Defining the thermodynamic force, X_i, in joules/mole.cm., as

$$X_i = \text{grad}(-\tilde{\mu}_i) \qquad (2.10)$$

then equation (2.9) becomes

$$\Phi = \sum_{i=1}^{n} J_i X_i \qquad (2.11)$$

where J_i is the mass-fixed flow of species i in moles/cm^2.sec.

2.3 Frames of Reference for Flows: The flows of equation(2.11) are defined arbitrarily in terms of a mass-fixed frame of reference. Since the systems are in mechanical equilibrium, any frame of reference may be chosen,[49] the choice depending on the purpose of study.

For binary electrolyte solutions, the solvent-fixed frame of reference is more convenient than, for example, the volume- or mass-fixed reference frames. Transformations exist for conversion from one frame of reference to another.[63,79,106,186]

For a binary electrolyte solution consisting of cation,1, anion,2, of valencies z_1 and z_2 respectively, and solvent,0,

equation (2.11) becomes

$$\Phi = J_1X_1 + J_2X_2 + J_0X_0 \qquad (2.12)$$

For the one-dimensional case, which is the normal experimental situation, equation (2.10) may be written as:

$$X_i = -\frac{\delta\tilde{\mu}_i}{\delta x} = -\left[\frac{\delta\mu_i}{\delta x} + z_i F\frac{\delta\psi}{\delta x}\right] \qquad (2.13)$$

omitting negligible gravitational terms. In equation (2.13), μ_i is the chemical part of the electrochemical potential in joules/mole, z_i is the signed valency, F is the Faraday in coulombs/equivalent, ψ is the electrical potential in volts, and x is the distance parameter in cm.

The X_i are not independent due to the Gibbs-Duhem equation, which may be written

$$\sum_{i=0}^{n} c_iX_i = 0 \qquad (2.14)$$

where c_i is the concentration of constituent i in moles/litre. Using equation (2.14) and eliminating the solvent term, equation (2.12) becomes:

$$\Phi = (J_1-c_1J_0/c_0)X_1 + (J_2-c_2J_0/c_0)X_2 \qquad (2.15)$$

The flow, J_i, of species i is given by the product of concentration, c_i, and velocity, v_i.

$$J_i = c_iv_i$$

Thus the terms $(J_i-c_iJ_0/c_0)$ in equation(2.15) are the flows of species i relative to the solvent 0, and are denoted by J_i^0.

$$J_i^0 = c_i(v_i-v_0)$$

The dissipation function may therefore be represented by two flows, J_1^0 and J_2^0, and their conjugate forces X_1 and X_2.

$$\Phi = J_1^0 X_1 + J_2^0 X_2$$

Since only solvent-fixed flows are considered, all flows will henceforth be denoted simply by J_i.

2.4 Phenomenological Equations and the ORR: In a system close to equilibrium, the flows and forces are linearly related by phenomenological equations which may be written as:[107]

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \qquad i=1,2,\ldots,n \qquad (2.16)$$

The L_{ij} are phenomenological coefficients, and are independent of the X_j. They convey the possibility of cross-effects between irreversible phenomena, since each flow may be a linear function of all the thermodynamic forces in the system. The flows J_i will be affected by the other forces in the system provided the L_{ij} ($i \neq j$) are non-zero. These L_{ij} are a measure of the degree to which a flow of one species is affected by forces on other species in the system, and are the cross- or coupling-coefficients.

Where the L_{ij} are zero, the direct coefficients L_{ii} are a specific measure of the mobility of species i. From the general definition of a force equation, the L_{ii} provide the linear relation between flow and conjugate force described by simple laws such as those of Ohm and Fick.

To fully characterise a system of n forces and flows, n^2 phenomenological coefficients are required. However, symmetry requirements shown by Onsager[130], using statistical mechanics, state that

$$L_{ij} = L_{ji} \qquad i,j = 1,2,\ldots,n \qquad (2.17)$$

The relations (2.17) are known as the Onsager Reciprocal Relations (ORR) and as a result the number of coefficients necessary to characterise a system is reduced from n^2 to $\frac{1}{2}n(n+1)$. The ORR have been verified experimentally for a large

number of phenomena.[107,110,111] The L_{ij} are constrained by the inequality

$$L_{ii} \cdot L_{jj} \geq (L_{ij})^2$$

which states that the direct coefficients must be positive, though the cross-coefficients may be either positive or negative.

The direct coefficients, L_{ii} and L_{jj}, are a measure of the mobility which an ion would have in the absence of interactions with oppositely-charged ions. The L_{ij} ($i \neq j$) are the mobility interaction coefficients and are a direct measure of the cation-anion kinetic coupling.

Both the L_{ii} and L_{ij} are dependent upon the frame of reference. In the case of a solvent-fixed reference frame, they also include contributions from the solvent.

2.5 Alternative Representation: the R_{ij}. Irreversible processes in electrolytes may be considered using the inverse formulation of friction coefficients, R_{ij}.[10,82,83,108]

The linear laws for the inverse description are:

$$X_i = \sum_{j=0}^{n} J_j R_{ij} \qquad i=0,1,\ldots,n \qquad (2.18)$$

where the X_i are those of equation (2.13) and the R_{ij} are obtained by matrix inversion of the L_{ij}.

Since neither the X_i nor the J_i are independent, the R_{ij} are not uniquely specified[87] unless the assumption is made that[108]

$$\sum_{j=0}^{n} c_j R_{ij} = 0 \qquad i=0,1,\ldots,n \qquad (2.19)$$

With this assumption, the R_{ij} may be shown to be reference-frame independent.[79]

The R_{ij} also obey the ORR;[106,142,144]

$$R_{ij} = R_{ji} \qquad i,j=0,1,\ldots,n \qquad (2.20)$$

and are constrained by the inequality

$$R_{ii} \cdot R_{jj} \geq (R_{ij})^2 \qquad (2.21)$$

R_{ii} is interpreted as the sum of all friction between species i and other species in the system. R_{ij} $(i \neq j)$ represents the frictional interaction between species i and species j.

2.7 L$_{ij}$ and R$_{ij}$ in terms of Measurable Quantities: For a binary electrolyte in a neutral solvent, three transport experiments must be performed in order to calculate L_{11}, L_{22}, and L_{12} $(=L_{21})$.

Consider an electrolyte AB which dissociates as

$$A_{\gamma_1} B_{\gamma_2} \longrightarrow \gamma_1 A^{z}1 + \gamma_2 B^{z}2$$

where A and B are cation and anion, z_1 and z_2 their signed valencies, and γ_1 and γ_2 the stoichiometric ionisation coefficients. Since there is equilibrium,

$$\mu_{12} = \gamma_1 \mu_1 + \gamma_2 \mu_2 \qquad (2.22)$$

where μ_{12} is the chemical potential of the electrolyte.

Conservation of charge requires that

$$\gamma_1 z_1 + \gamma_2 z_2 = 0 \qquad (2.23)$$

The phenomenological equations for this system are given by equation (2.16).

$$\begin{aligned} J_1 &= L_{11} X_1 + L_{12} X_2 \\ J_2 &= L_{21} X_1 + L_{22} X_2 \end{aligned} \qquad (2.24)$$

Four transport quantities are accessible experimentally, namely conductance, Λ, diffusion, D, Hittorf transference number, t^h, and emf or cell transference number, t^c.

2.7.1 Conductance: In conductivity experiments, the external applied force is electrical potential gradient only, and, since concentration is uniform, there are no gradients of chemical potential.

Thus

$$X_i = -z_i F(\partial\psi/\partial x) \qquad (2.25)$$

When an electric current is passed through the solution, the current density I in amp./cm.^{2} is given by:

$$I = (z_1 J_1 + z_2 J_2).F \qquad (2.26)$$

Substituting for J_1 and J_2 from equations (2.24) and using equation (2.25) for X_1 and X_2, equation (2.26) becomes

$$I = F^2(-\partial\psi/\partial x)[\ z_1^2 L_{11} + z_1 z_2(L_{12}+L_{21}) + z_2^2 L_{22}\ ] \qquad (2.27)$$

Ohm's Law states that

$$I = k(-\partial\psi/\partial x) \qquad (2.28)$$

where k is the specific conductivity in (ohm cm.)$^{-1}$, and substitution of equation (2.28) into equation (2.27) gives

$$k = F^2.\alpha \qquad (2.29)$$

where

$$\alpha = [\ z_1^2 L_{11} + z_1 z_2(L_{12}+L_{21}) + z_2^2 L_{22}\ ] \qquad (2.30)$$

Substitution of equation (2.29) into the expression for equivalent conductance, Λ, yields

$$\Lambda = 10^3 F^2 \alpha/N \qquad (2.31)$$

where N is the concentration in equivalents/litre.

Λ is measured on an apparatus-fixed frame of reference, but may be shown to have the same value in any reference frame.[108]

2.7.2 Hittorf Transference Number, t^h. t_i^h is defined as the fraction of the total current carried by the ith ion relative to the solvent when a current I is passed through a solution of uniform composition, and may be written

$$t_i^h = z_i F J_i / I$$

Since the composition is uniform, the forces X_1 and X_2 are given by equation (2.25). Use of this expression with equations (2.26) and (2.24) gives, for ion i,

$$t_1^h = (z_1^2 L_{11} + z_1 z_2 L_{12})/\alpha \qquad (2.32a)$$

and similarly

$$t_2^h = (z_2^2 L_{22} + z_1 z_2 L_{12})/\alpha \qquad (2.32b)$$

2.7.3 Emf Transference Number, t^c. An electrochemical cell having identical electrodes and a single electrolyte, but which has a varying composition, may be represented by, for example

$$Pb \mid PbCl_2(m_1) \;\vdots\; PbCl_2(m_2) \mid Pb$$

where m_i is molality , and $m_2 > m_1$.

In this system diffusion will take place, and a charge separation will be induced owing to the different ionic mobilities. After a very short time, of the order of a nanosecond,[53] coulombic forces come into effect, with the result that no net current flows through the solution, and therefore

$$I = (z_1 J_1 + z_2 J_2).F = 0 \qquad (2.33)$$

In this situation, both the gradient of chemical potential, $\partial \mu_i / \partial x$, and the gradient of electrical potential, $\partial \psi / \partial x$, are non-zero.

Substituting equations (2.13) and (2.24) in equation (2.33),

$$F.(-\partial\psi/\partial x) = (t_1^c/z_1).(\partial\mu_1/\partial x) + (t_2^c/z_2).(\partial\mu_2/\partial x) \qquad (2.34)$$

where $(-\partial\psi/\partial x)$ is the gradient of liquid junction or diffusion potential, and t_1^c is defined as:

$$t_1^c = (z_1^2 L_{11} + z_1 z_2 L_{21})/\alpha \qquad (2.35)$$

with a corresponding expression for t_2^c.

Inspection of equations (2.35) and (2.32a) shows that t_1^c and t_1^h are identical only if $L_{12} = L_{21}$, that is, only if the ORR are valid.

2.7.4 Salt Diffusion: If two solutions of different concentrations are brought into contact, diffusion will occur as the system seeks to establish equilibrium. The term $\partial\mu_i/\partial x$ is non-zero and no current flows.

From equations (2.23) and (2.33),

$$J_1/\gamma_1 = J_2/\gamma_2 = J_s \qquad (2.36)$$

where J_s is the solvent-fixed flow of the electrolyte as a whole. The diffusion coefficients for a binary electrolyte system are defined[108] by:

$$J_s = -(D_0/1000).(\partial c/\partial x) = -L.(\partial\mu_{12}/\partial x) \qquad (2.37)$$

where D_0 is the solvent-fixed diffusion coefficient in $cm^2/sec.$ and L is the thermodynamic diffusion coefficient in $moles^2/$ joule sec.cm. Equation (2.37) may be rewritten as

$$(D_0/1000).(\partial c/\partial x) = L.(\partial\mu_{12}/\partial c).(\partial c/\partial x) \qquad (2.38)$$

and so

$$L = (D_0/1000).(\partial\mu_{12}/\partial c) \qquad (2.39)$$

Using equation (2.39) and the expansion

$$\partial\mu_{12}/\partial c = RT\gamma(1+c\,d\ln y/dc)/c$$

where $\gamma = \gamma_1 + \gamma_2$ and y is the mean molar activity coefficient, equation (2.37) becomes

$$J_s = (-\partial\mu_{12}/\partial x).D_0 c/1000RT\gamma(1+c\,d\ln y/dc) \qquad (2.40)$$

From equations (2.13),(2.22),(2.24),(2.33), and (2.34), and some manipulation,

$$J_s = (\partial\mu_{12}/\partial x).(z_1 z_2/\gamma_1\gamma_2).(L_{11}L_{22}-L_{12}^2)/\alpha \qquad (2.41)$$

Comparison of equations (2.40) and (2.41) gives

$$D_0 = -(1000RT\gamma z_1 z_2/c\gamma_1\gamma_2).(1+c\,d\ln y/dc).(L_{11}L_{22}-L_{12}^2)/\alpha \qquad (2.42)$$

where α is as defined by equation (2.30).

In the literature, volume-fixed diffusion coefficients, D_v, and mean molal activity coefficients, f, are reported. It may be shown[108] that

$$D_0/(1+c\,d\ln y/dc) = D_v/(1+m\,d\ln f/dm) \qquad (2.43)$$

where m is the molality. Substitution of equation (2.43) in equation (2.42) gives:

$$D_v = -(1000RT\gamma z_1 z_2/c\gamma_1\gamma_2).(1+m\,d\ln f/dm).(L_{11}L_{22}-L_{12}^2)/\alpha \qquad (2.44)$$

Equations (2.31), (2.32a), (2.35), and (2.44) may be solved simultaneously to give an expression for the L_{ij} in terms of the quantities Λ, t_i^h, t_i^c, and D_v. If the ORR are assumed, then $t_i^h = t_i^c$, and the resulting equation is:

$$L_{ij}/N = (t_i t_j \Lambda/1000F^2 z_i z_j) + \gamma_i\gamma_j D_v/1000RT\gamma z_1(1+m\,d\ln f/dm) \qquad (2.45)$$

If F is in coulombs/equivalent, R is in joules/mole deg., and D_v is in cm^2/sec., then L_{ij} has units of $moles^2$/joule sec. cm.

The R_{ij} are obtained by matrix inversion of the L_{ij}. For any system,

$$R_{ij} = |L_{ij}| / |L|$$

where $|L_{ij}|$ is the minor of L_{ij} and $|L|$ is the determinant of the L-coefficient matrix. The coefficients R_{i0} are obtained from R_{ij} using the relations defined in equation (2.19),

$$\sum_{j=0}^{n} c_j R_{ij} = 0 \qquad (i = 0,1,2)$$

where c_0 is the concentration of solvent given by

$$c_0 = 1000c/mM_0 \qquad (2.46)$$

where M_0 is the molecular weight of the solvent. The units of R_{ij} are joule sec.cm./moles^2.

For a binary electrolyte solution on a solvent-fixed frame of reference, equation (2.18) becomes

$$\begin{aligned} X_1 &= R_{11}J_1 + R_{12}J_2 \\ X_2 &= R_{21}J_1 + R_{22}J_2 \end{aligned} \qquad (2.47)$$

From equations (2.19) and (2.47), and assuming $c_1 = c_2$, R_{11} and R_{22} may be eliminated to give

$$\begin{aligned} X_1 &= -R_{12}(J_1-J_2)-(c_0/c_1)R_{10}J_1 \\ X_2 &= -R_{21}(J_2-J_1)-(c_0/c_2)R_{20}J_2 \end{aligned} \qquad (2.48)$$

where R_{12} $(=R_{21})$ and R_{i0} $(i=1,2)$ represent friction between ion and ion, and ion and water respectively.

Expressions for R_{ij} in terms of experimental quantities may be derived in the same way the L_{ij} were obtained. Using the ORR, the results are [108]

$$L = -(c/c_0).(\gamma_1 R_{10}+\gamma_2 R_{20}) = (c/c_0)^2 R_{00} \qquad (2.49)$$

$$t_1 = \gamma_2 R_{20}/(\gamma_1 R_{10} + \gamma_2 R_{20}) \qquad (2.50)$$

$$\alpha = z_1 z_2 c(\gamma_1 R_{10} + \gamma_2 R_{20})/(c_0 R_{10} R_{20} + c R_{12}(\gamma_1 R_{10} + \gamma_2 R_{20})) \qquad (2.51)$$

where $c = c_i/\gamma_i$ and c_0 is defined by equation (2.46).

Solution of equations (2.49), (2.50), and (2.51) leads to the explicit expressions for R_{ij}.

$$R_{11} = z_1^2/\alpha + t_2^2/\gamma_1^2 L \qquad R_{22} = z_2^2/\alpha + t_1^2/\gamma_2^2 L$$

$$R_{12} = z_1 z_2/\alpha + t_1 t_2/\gamma_1 \gamma_2 L \qquad R_{00} = (c/c_0)^2/L \qquad (2.52)$$

$$R_{10} = -(c/c_0).(t_2/\gamma_1 L) \qquad R_{20} = -(c/c_0).(t_1/\gamma_2 L)$$

2.8 Self Diffusion: The term 'self-diffusion' refers to an unattainable ideal, since true self-diffusion cannot be detected owing to the indistinguishability of the molecules. A process closely related to self-diffusion occurs when an ion or species present in trace amount diffuses in a large excess of electrolyte. This process is termed isotopic- or tracer-diffusion; an example is the diffusion of radioactive chloride ion present in trace amounts in an otherwise uniform solution of sodium chloride. The isotopic species present differs from the 'normal' isotope only enough to be distinguishable; all physical and electrical properties of the solution are unchanged.

2.8.1 Mass Effects. It is generally believed[120,167] that the mobilities of ions and molecules are more closely related to size and shape than to mass. This is exemplified by the virtual equalities of the mobilities of chloride and iodide ions in aqueous solution although their masses differ by a factor of four. Thus it is to be expected that isotope effects due to mass differences should be small, if not negligible, when trace-ion diffusion is involved. Some studies by Pikal[143]

using Na^{22} and Na^{24} tracers in aqueous solutions of NaCl and LiBr have indicated the presence of a small isotope effect of the order of a few tenths of a percent, but since this is close to the limits of experimental precision, no firm conclusions may be drawn, save that any effect is small.

In the case of the isotopic diffusion of water, however, considerable evidence suggests that isotope effects are large, since diffusion coefficients of water labelled with different isotopes have differed by up to 15%. This point will be discussed more fully in chapter 4.

The assumption, then, that ionic isotope diffusion is identical to self-diffusion is in general very good. The driving force for isotope diffusion is the gradient of (RTlnc), since the ionic environment of the tracer ion is effectively unchanged during diffusion and hence its activity coefficient may be regarded as constant.

Consider a binary electrolyte system, for which the phenomenological equations are given by equation (2.47).

$$\begin{aligned} X_1 &= R_{11}J_1 + R_{12}J_2 \\ X_2 &= R_{21}J_1 + R_{22}J_2 \end{aligned} \qquad (2.47)$$

Let the tracer ion be the cation, then the system becomes the simplest case of a ternary solution, for which the phenomenological equations become:

$$x_1 = r_{11}j_1 + r_{12}j_2 + r_{11'}j_{1'} \qquad (2.53a)$$

$$x_2 = r_{21}j_1 + r_{22}j_2 + r_{21'}j_{1'} \qquad (2.53b)$$

$$x_{1'} = r_{1'1}j_1 + r_{1'2}j_2 + r_{1'1'}j_{1'} \qquad (2.53c)$$

where the label 1' refers to the tracer ion.

If species 1' is chemically identical to the bulk species 1, then, for the same transport experiment,

$$J_1 = j_1 + j_{1'}\,; \qquad J_2 = j_2\,; \qquad X_2 = x_2\,;$$

and, since $C_1 = c_1 + c_{1'}$, where C_1 is the total concentration of species of type 1,

$$C_1 X_1 = c_1 x_1 + c_{1'} x_{1'} \qquad (2.54)$$

Furthermore, since the isotopes are identical,

$$C_1 R_{11} = c_1 r_{11} + c_{1'} r_{11'} \qquad (2.55)$$

Under conditions of self-diffusion,

$$J_1 = j_1 + j_{1'} = 0 \qquad (2.56)$$

and using equations (2.13) and (2.53a)

$$j_1 = (-\partial c/\partial x) \cdot RT/c_1(r_{11} - r_{11'}) \qquad (2.57)$$

Since the species 1' is present in vanishingly small amounts, then the approximation

$$C_1 \cong c_1$$

is a good one, and, with equation (2.55), equation (2.57) becomes:

$$j_1 = (-\partial c/\partial x) \cdot RT/C_1(R_{11} - r_{11'}) \qquad (2.58)$$

Comparison of equation (2.58) with Fick's Law gives

$$D_{11} = RT/C_1(R_{11} - r_{11'}) \qquad (2.59)$$

or, in general

$$D_{ii} = RT/C_i(R_{ii} - r_{ii'}) \qquad i=0,1,2 \qquad (2.60)$$

Thus the self- or isotopic diffusion coefficient of a species may be related to the value of R_{ii} in the correspond-

ing binary solution.

The derivation of equation (2.60) in terms of L_{ij} gives

$$D_{ii} = RT[(L_{ii}/C_i)-(C_i/c_i)(l_{ii'}/c_{i'})] \qquad (2.61)$$

However, the description of isotopic diffusion coefficients in terms of R_{ij} coefficients is preferred for certain reasons. Both the R_{ij} and D_{ii} are independent of the frame of reference chosen. However, the L_{ij} are with respect to a solvent-fixed reference frame, and so the quantity $l_{ii'}$ must correct for frame of reference and include specific isotope-isotope terms. Thus $l_{ii'}$ is intrinsically more complex a quantity than $r_{ii'}$. Also, since R-coefficients are analogous to the concept of mechanical friction between species,[29,67] they are therefore more meaningful physically.

CHAPTER 3

ISOTOPIC DIFFUSION STUDIES

3.1 Introduction

The purpose of this work was to complete the ionic diffusion data for the entire alkali metal chloride series, with the exception of Rb^+ ion in RbCl solution, for which no suitable isotope existed for study under our laboratory conditions. A large quantity of data for the alkali metal chloride-water systems was already available in the literature; only data for Cs^+ ion in CsCl, and for Cl^- ion in RbCl and CsCl was missing.

The study of water diffusion using an isotopically labelled form of water, tritiated water, was seen as a natural extension of earlier work by Jalota [66] on an irreversible thermodynamic analysis of the series of alkali metal chloride-water systems.

3.2 Methods Applied to the Study of Isotopic Diffusion in Liquid Systems. Isotopic diffusion experiments do not involve bulk concentration gradients, since the isotopic species is present in negligible quantity, and the bulk physical properties of the solution, such as density, conductivity, etc., are unchanged by the addition of isotope. When the isotopic species is present in substantial quantities, as, for example, in the case of interdiffusion of D_2O-H_2O mixtures studied by Longsworth,[94] then the physical properties of the solutions are altered, and methods which exploit these differences may be used.

In general, however, the experimental methods available for the study of isotopic diffusion have been developed specifically for this purpose, or are modifications of pre-existing methods used in the study of bulk salt diffusion.

The method used in this work was a Stokes-type diaphragm cell. Previous work in this laboratory[29,67] on salt diffusion studies had indicated that a precision of $\pm 0.2\%$ was readily obtainablewith this apparatus. As the diaphragm cell is readily adaptable to the study of isotopic diffusion, this method was selected for the study of isotope diffusion in aqueous solutions of the alkali chlorides.

A brief outline of the alternative methods available is given below.

3.2.1 The Open-Ended Capillary Method. This method, normally referred to simply as the capillary method, was developed specifically for isotope diffusion studies by Anderson and Saddington,[4] and later modified by Mills.[115] A general description of the method is given by Wang [178] and by Robinson and Stokes.[152]

This is theoretically an absolute method, but in practice some form of calibration has been found necessary,[112] since in many cases inaccurate data have been obtained. Convectional disturbances at the junction of the capillary mouth and the external bath solution can give rise to two separate sources of error.

The immersion effect[81,112,113] occurs on lowering a capillary tube into the bath solution, when convectional removal of radioactivity can result in a loss of 0.5-2% of the contents of the capillary. This effect can be minimised if suitable precautions are taken.[116]

The other effect arises from the necessity of maintaining a flow of bath solution across the capillary mouth. This flow can give rise to turbulence at the capillary end which can scoop out the contents of the capillary, thereby reducing the effective length, l, of the diffusion column. Since one of the boundary conditions for the solution of Fick's Second Law,

$$\partial c_i/\partial t = D_i \partial^2 c_i/\partial x^2$$

which is applicable to capillary diffusion, may be expressed as $c_i=0$ for $x>l$, then the above effect was termed the 'Δl effect' by Wang[179] and gives rise to high results. Mills,[114] however, has shown that this effect can also be minimised by careful experimental technique.

Further errors can arise from failure to remove completely all traces of radioactive solution from the capillary for analysis at the end of an experiment. Mills,[115] and independently Thomas,[171] circumvented this problem by encasing the capillary tube in a scintillation-counter crystal and measuring the decrease in activity continuously for the duration of the experiment.

Measurements by this continuous-monitoring method have yielded isotopic diffusion coefficients to a precision of the order of $\pm$0.2%.[116]

3.2.2 The Radiometric Porous Frit Method. This method was adapted from the porous frit method of Wall, Grieger and Childers[177] and was adapted specifically for isotope diffusion studies by Nelson.[126] Subsequent use has been chiefly by Marcinkowsky and coworkers.[96-99]

In this method, small slabs of porous material, such as unglazed porcelain or gold frits, are equilibrated in a solution containing a small quantity of radioactive isotope.

The slabs or frits are then transferred to a bath containing the same solution but with the isotope absent. The isotopic diffusion coefficient may be calculated from the decrease in activity with time.

This method also requires calibration with some electrolyte for which reliable diffusion data exist. Though rapid, the precision of the method is limited to a few percent.

3.2.3 The Spin-Echo NMR Method. Nuclear magnetic spin echoes were discovered by Hahn [54] in 1950. The subsequent theoretical analysis by Das and Saha,[25] and Carr and Purcell [17] led to the development of the method by a number of workers.[28,30,31,40,145] A full account of the method is given by Douglass and McCall.[27]

The advantages of spin-echo nmr are that the method does not require the presence of unusual isotopes, and self-diffusion measurements may be made rapidly under a wide variety of experimental conditions. Precision, however, is limited to 2-3% in most cases, though an uncertainty of only ±1% has been achieved.[145]

3.3 The Stokes Diaphragm Cell Method. This method was introduced by Northrop and Anson,[128] though its modern form is mainly attributable to Stokes,[165] with minor modifications by other workers.[60,102,123,124] The method is not absolute; the diffusion cell must be calibrated using a standard electrolyte, normally potassium chloride, for which diffusion coefficients are already known.[57] This technique has been widely used in the study of bulk salt diffusion, and was first adapted for isotopic diffusion measurements by Adamson.[1]

This method initially suffered from a number of disadvantages, though these have now been largely eliminated.

The effects of vibration and small temperature fluctuations are virtually eliminated by confining the diffusion process to the narrow capillary pores of a sintered glass diaphragm. This introduces other difficulties, however, since these conditions necessitate uniform concentrations in the reservoirs above and below the diaphragm up to the diaphragm surface. This in turn requires stirring of the solutions in

the reservoir to remove any stagnant layers of solution near the diaphragm surfaces. The system of stirring adopted by Stokes consisted of two soft iron wires sealed in thin glass tubes and situated just above and below the diaphragm surfaces. These stirrers were rotated magnetically by an external stirring mechanism.

It is important that the diaphragm be horizontal, within 2-3°, since any departure from the horizontal causes errors in the measured diffusion coefficients due to bulk flow through the diaphragm. The amount of bulk flow increases as an approximately quadratic function of the angle by which the diaphragm departs from the horizontal.[165] Bulk flow due to density gradients is eliminated by having the more dense solution on the lower side of the diaphragm.

The effect of variation in stirring speed has been investigated by Stokes,[165] Fell,[32] Neilsen et al.,[125] and Mills.[114] Stokes has shown that, above a 'threshold' rate of approximately 25rpm, the stirring speed has no effect on the measured diffusion coefficients. Stokes found this to be true over the range 25-80rpm, as did Mills[114] over the range 60-110rpm.

The main limitation on the use of diaphragm cells for the study of diffusion in liquid systems is due to solute adsorption on the diaphragm pore walls. This gives rise to an anomalously rapid transport mechanism through the diaphragm[2,124,165] which becomes increasingly important as the concentration decreases below 0.01N[60,124] and leads to erroneous results. For this reason, the diaphragm cell technique is restricted to solutions more concentrated than 0.05N.

3.3.1 Theoretical Considerations. The diaphragm cell method is a steady-state method based on Fick's First Law of Diffusion:[33]

$$J = D(-\partial c/\partial x) \qquad (3.1)$$

In true steady-state diffusion, a constant concentration is maintained at both ends of a column of diffusing liquid and the flux of solute ultimately becomes independent of

time and of position in the column. This situation is termed the steady state, and measurement of the flux, J, and concentration gradient, $(\partial c/\partial x)$, gives the diffusion coefficient, D, from equation (3.1).

The experimental difficulties of establishing and maintaining a true steady state have prevented widespread use of this method; only Clack[20] having obtained results in this way.

In the diaphragm cell method, diffusion is confined to the capillary pores of the diaphragm. However, as the diffusion process reduces the concentration difference, the flux of solute across any plane in the diaphragm parallel to the upper and lower surfaces will decrease slowly with time. For this reason, a 'pseudo' steady state is said to be established.

Let the concentrations of solutions at the beginning and end of an experiment be denoted by c_1, c_2, c_3, and c_4, and the volumes of the compartments and diaphragm be V_1, V_2 and V_3 respectively. Let the total effective cross-section and average length of the diaphragm pores be A and l respectively.

Denoting the flux of solute by J(t), since it is a function of time, and if the concentrations of the upper and lower compartments are denoted by c' and c'' respectively, then the rates of change of the concentrations are related to J(t) by

$$dc'/dt = -J(t).A/V_1 \quad \text{and} \quad dc''/dt = +J(t).A/V_2 \qquad (3.2)$$

hence

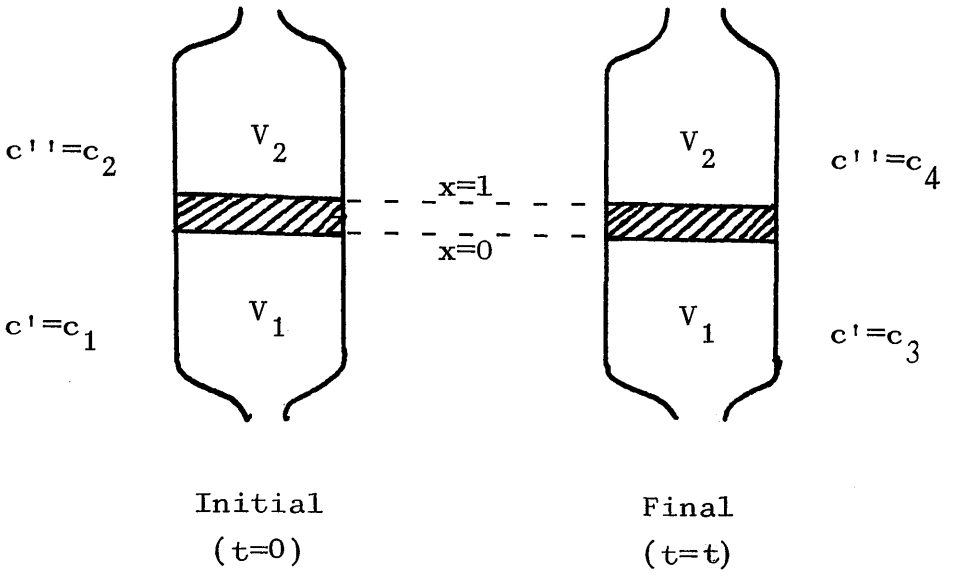
$$d(c'-c'')/dt = -J(t).A.(1/V_1 + 1/V_2) \qquad (3.3)$$

The average value of the diffusion coefficient with respect to concentration over the range c' to c'', $\bar{D}(t)$, is also a function of time

$$\bar{D}(t) = (1/(c'-c'')).\int_{c''}^{c'} D.dc \qquad (3.4)$$

$$= -(1/(c'-c'')).\int_0^1 D.(\partial c/\partial x).dx \qquad (3.5)$$

Figure 3.1



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where x is the distance of the plane considered from the lower surface of the diaphragm.

Combination of equations (3.1) and (3.5) gives, upon integration,

$$\overline{D}(t) = J(t).1/(c'-c'') \qquad (3.6)$$

which, when combined with equation (3.3), becomes:

$$-\, d\ \ln(c'-c'')/dt = \overline{D}(t).(1/V_1 + 1/V_2).A/1 \qquad (3.7)$$

Integrating equation (3.7) between the limits shown in Figure 3.1,

$$\ln\left[(c_1-c_2)/(c_3-c_4)\right] = (A/1).(1/V_1 + 1/V_2).\int_0^t \overline{D}(t).dt \qquad (3.8)$$

Defining a further time-averaged diffusion coefficient by $\overline{D}$, where

$$\overline{D} = (1/t).\int_0^t \overline{D}(t).dt \qquad (3.9)$$

then equation (3.8) becomes:

$$\overline{D} = (1/\beta t).\ln(c_1-c_2/c_3-c_4) \qquad (3.10)$$

where $\beta = (A/l).(1/V_1 + 1/V_2)$, and is termed the cell constant. The $\bar{D}$ calculated from equation (3.10) are integral diffusion coefficients, which are converted to the more fundamental differential diffusion coefficients,* D.

Substitution of the relation

$$\bar{D} = (1/(c'_m - c''_m)).\int_{c''_m}^{c'_m} D.dc \qquad (3.11)$$

where

$$c'_m = (c_1 + c_3)/2 \quad \text{and} \quad c''_m = (c_2 + c_4)/2$$

instead of the more exact equation (3.9) has been shown[42] to introduce negligible error.

Equation (3.11) treats the integrand as having a constant value equal to its value when the concentrations c' and c'' are half-way between their initial and final values.

The integral diffusion coefficient $\bar{D}$ corresponding to the initial and final concentrations is calculated by defining a quantity $\bar{D}^0(c)$ as the average D with respect to concentration over the range 0 to c.

$$\bar{D}^0(c) = (1/c).\int_0^c D.dc \qquad (3.12)$$

Combination of equations (3.11) and (3.12) gives:

$$\bar{D} = (1/(c'_m - c''_m)).[\ c'_m.\bar{D}^0(c'_m) - c''_m.\bar{D}^0(c''_m)\ ] \qquad (3.13)$$

The quantity $\bar{D}^0(c)$ for potassium chloride solutions is available[166] from the D values of Harned and Nuttall,[57] and Gosting.[44]

For a set of mean concentrations, c'_m and c''_m, of a diffusion experiment, $\bar{D}^0(c'_m)$ and $\bar{D}^0(c''_m)$ were obtained using an empirical fit between $\bar{D}^0(c)$ and c. These values were then substituted into equation (3.13) to give $\bar{D}$. Substitution of

* Where concentration gradients are absent, as in the case of isotope diffusion, $\bar{D}$ and D are identical. This may be verified by inspection of equation (3.4).

$\overline{D}$ in equation (3.10) gave a value for the cell constant.

By inspection of equation (3.10), the units of c do not affect the value of $\overline{D}$. Thus in cell calibration experiments, concentrations were used to calculate $\overline{D}$, whereas counting rates were used in isotopic diffusion experiments.

3.3.2 The Diaphragm Cell. The diaphragm cell is shown schematically in Figure 3.2.

The cell was of Pyrex glass, the two compartments having approximately equal volumes. The diaphragms, obtained commercially, were of sintered glass of porosity 4 (average pore diameter 10-15μ).

Each compartment contained a glass stirrer designed according to Stokes.[165] The lengths of the stirrers were typically 3-4 mm. less than the diameter of the diaphragm to ensure that as much of the diaphragm surface as possible was stirred, and also to facilitate their removal from the diffusion cell.

The cell was closed by capillary tubes 2 mm. in diameter accommodated in Quickfit-type stoppers. The lower stopper incorporated a high-vacuum quality Teflon stopcock.

Two such cells were used; their dimensions are given in Table (3.1).

The cell volumes, V_1,V_2, and V_3, were determined by weighing the cell dry and then weighing the cell with the various compartments filled in turn with distilled water at 25°C. All weighings were carried out with the cell fully assembled and with both stirrers in position. Normal vacuum corrections were applied to all weights. The volumes reported in Table (3.1) are the averages of three determinations, to an estimated accuracy of $\pm$0.15%.

3.3.3 The External Stirring Mechanism. The mechanism is shown in Figure 3.3. Four bar magnets were fitted into the holders attached to the arms of the brass assembly. The position of each holder could be adjusted independently of the other three, making it possible to alter the positions of the stirrers in the cell in such a way that they rotated

Figure 3.2 The diaphragm cell.

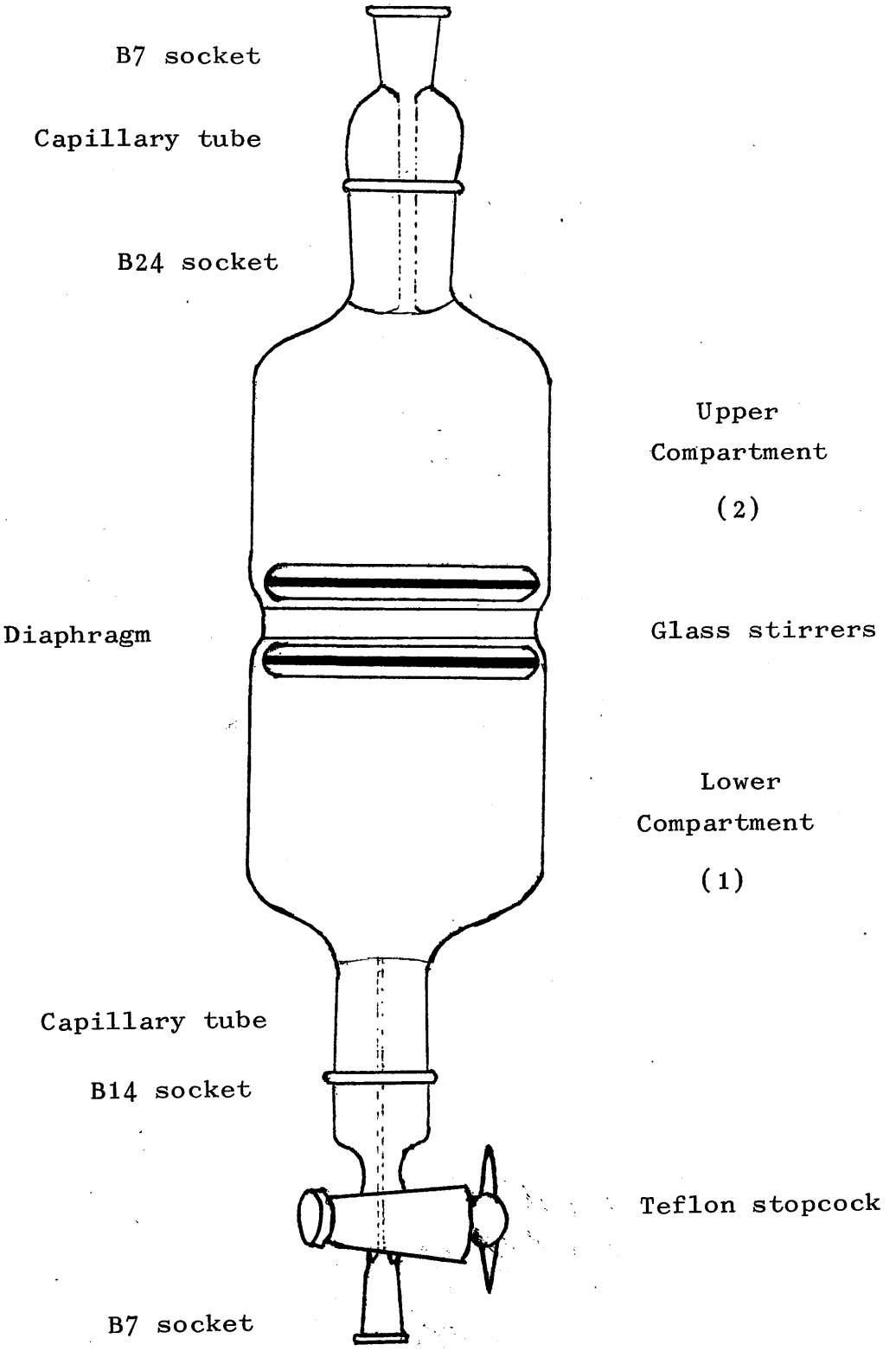
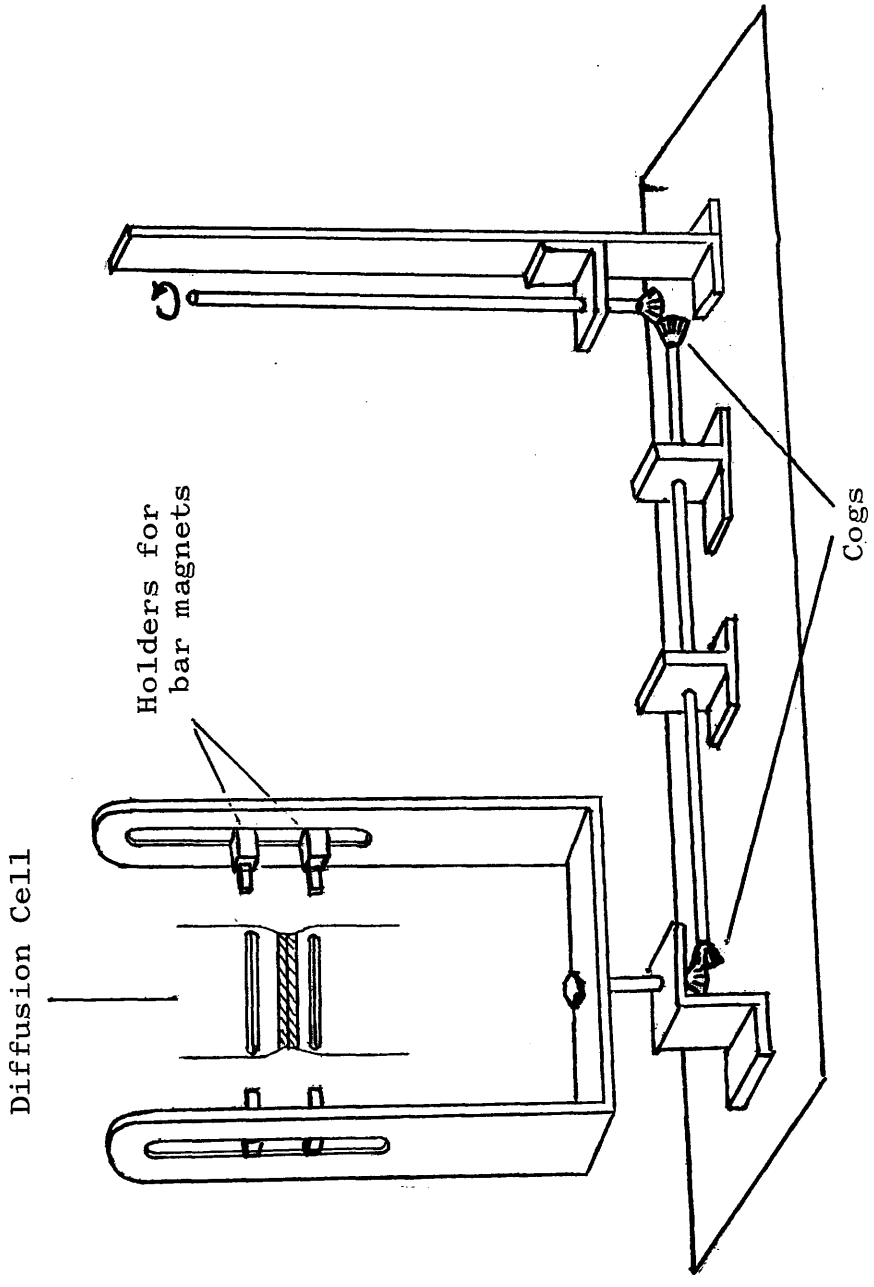


Table (3.1). Dimensions of the experimental diffusion cells.

	Cell 1	Cell 2
V_1	53.31ml.	95.60ml.
V_2	60.63ml.	108.53ml.
V_3	2.07ml.	3.59ml.
V^{**}	1.1347	1.1327
Diameter of diaphragm	40mm.	50mm.
Thickness of diaphragm	2.5mm.	5mm.
Length of stirrers	37mm.	47mm.
Cell constant, β	0.47521	0.17256

** $V = (V_2+V_3/2)/(V_1+V_3/2)$.

Figure 3.3 The external stirring mechanism.



one to two millimetres above and below the diaphragm surfaces. The motor and cog system were adjusted to give a constant stirring speed of 50-60rpm.

3.3.4 Filling of the Cell. All solutions used in diffusion experiments were filtered through a Millipore filter unit using a filter of 1.2μ pore size and then degassed under vacuum for 25-30 minutes prior to use. The filter disc was rinsed with $\sim$ 1 litre of distilled water prior to use to remove any traces of a detergent contaminant which sometimes occurs in such discs.

The cell was filled in a vertical position. Solution was poured into compartment 2 and drawn through the diaphragm under partial vacuum in order to saturate the diaphragm pores with solution and remove any trapped air bubbles. The compartment was stoppered, the cell was inverted, and compartment 1 was filled with solution.

In the case of cell calibration experiments, potassium chloride solution of $\sim$0.5M was used to saturate the diaphragm and to fill compartment 1. The cell was inverted and compartment 2 was filled with distilled water and stoppered.

In the case of isotope diffusion experiments, the same solution was used to fill both compartments and to saturate the diaphragm. After filling compartment 1, a small volume of isotopically labelled solution, typically 0.05-0.3 ml., was injected. This compartment was stoppered, the cell was inverted, and compartment 2 filled with solution and stoppered. All stoppers were coated with a thin film of Apiezon grease.

The filled cell was clamped vertically, with the diaphragm horizontal, in a water-filled bath maintained at 25°C $\pm$0.01, and stirring commenced.

In order to develop a linear concentration profile in the diaphragm, a prediffusion period is necessary. The time taken for such a profile to be established may be calculated approximately by means of the Gordon[38,42,119] inequality:

$$D\tau/l^2 > 1.2 \qquad (3.14)$$

where D is the diffusion coefficient in $cm.^2/sec.$, l is the 'apparent thickness' of the diaphragm, ($l \cong 1.6 \times$ true thickness), and τ is the prediffusion time in seconds. Use of equation (3.14) gives prediffusion times of approximately 2.5 hours and 10 hours for cells 1 and 2 respectively.

Pikal,[131] however, by using the equations of Barnes,[6] has shown that prediffusion times smaller by a factor of five than those given by the Gordon inequality may be employed without introducing serious error. Accordingly, prediffusion times of the order of two to three hours were used for both cells.

After this period, solution in the upper compartment was withdrawn into a 100 ml. pipette containing ~10 ml. of fresh solution. The compartment was rinsed thoroughly, filled with the mixed solution, and stoppered. The stirrer and electric timer were started immediately. The small amount of mixed solution remaining in the pipette was set aside for analysis.

In the original method of Stokes,[165] steady state conditions were achieved by a preliminary diffusion period of a few hours, after which time solution in the upper compartment was removed and replaced by fresh solution at the original concentration. The diffusion experiment was taken to begin from this time.

If the original concentration of solution be c_2, and the concentration after the prediffusion time be c_2', then clearly $c_2' > c_2$. However, steady state conditions pertain to c_2' and not to c_2, and this introduces a small error, the zero time error. The magnitude of this error is a function of the time of prediffusion and the magnitude of the diffusion coefficient.

With the procedure used in this work, the volume of solution of concentration c_2' was of the order of 60-100 ml., and the volume of solution of concentration c_2 was approximately 10 ml. Thus the concentration of the mixed solution at the beginning of an experiment was very close to c_2'. This procedure, suggested by Francesconi,[34] minimised the zero time error.

The normal duration of an experiment was approximately

46 hours, after which time solutions were removed from both compartments.

3.3.5 Analysis of Experimental Solutions. After each experiment, weighed samples of each solution were diluted to <0.1M and analysed conductimetrically.

Samples of radioactive solutions were withdrawn using Hamilton syringes fitted with Chaney adaptors to ensure the same volume was withdrawn each time. The volume of each sample was approximately 0.08 ml. and was reproducible to $\pm$0.1%. The phosphor used was that described by Bray [13] for aqueous samples. Samples were added to 10 ml. aliquots of the phosphor solution contained in special plastic vials. The samples were counted in a Nuclear Chicago Mark 1 Liquid Scintillation Spectrometer fitted with an automatic sample changer and print-out device.

The conditions of the experiments were arranged such that no activities of less than 100cpm above background were recorded. Samples were counted for at least 20 minutes, during which time sufficient counts were recorded to give a statistical error of $\pm$1% on the lower counts and $\pm$0.5% on the higher ones.

When precipitation occurred in the phosphor, as was the case when solutions more concentrated than ~1 Molar were sampled, the error in the count was increased two- or three-fold. In such cases a small volume of water, usually ~1 ml., was precisely measured into each vial to dissolve the precipitate and to ensure that any resultant quenching effect was the same for each sample. The efficiency of counting, as determined by using a radioactive standard solution, was greater than 90%.

Concentrations were calculated from measured conductances by the method of successive approximations. Polynomials of the type

$$Y = \sum_{i=0}^{n} a_i X^i \qquad (3.15)$$

were fitted between specific conductivity, k, and concent-

ration, and concentration and equivalent conductivity, Λ, using literature data.[18] The measured specific conductivity gave a value of c, which in turn gave a value of Λ. Substitution of this Λ in the equation

$$\Lambda = 1000k/c$$

gave an improved value of c. This cyclic process was continued until successive estimates of concentration differed by less than 0.02%.

The concentration of the original (undiluted) solution was calculated from the weight of solution and the weight of water added, by means of the density equations:

$$m/c = \sum_{i=0}^{n} a_i c^i \qquad \text{and} \qquad c/m = \sum_{i=0}^{n} b_i m^i \qquad (3.16)$$

Coefficients for equations (3.15) and (3.16) for the various salt systems, and the computer programme written to perform the calculation, are given in Appendixes 1 and 2 respectively.

The initial concentration on the lower side, c_1, is not directly measurable with this type of cell, since it changes during the prediffusion time. However, c_1 may be calculated from c_2, the final concentrations c_3 and c_4, and the volumes of the cell compartments and diaphragm using the fact that the total amount of solute in the cell must remain constant. c_1 is given by :

$$c_1 = c_3 + (c_4 - c_2)V$$

where V is a function of the volumes V_1, V_2, and V_3, and is usually termed the volume parameter.

$$V = (V_2+V_3/2)/(V_1+V_3/2)$$

As a further check of the method, the diffusion coefficients of Na^{22} in NaCl solutions were measured and the results compared with Mills'[118] data for this system.

3.3.6 Reagents. B.D.H. Analar grade NaCl and KCl were recrystallised twice from distilled water, dried in an oven at 130°C for 24 hours, and transferred to a vacuum desiccator over silica gel. Crystals were ground in an agate mortar, dried in an oven at 130°C for three days and finally stored in a vacuum desiccator over silica gel.

Spectroscopically pure LiCl and CsCl were obtained from Johnson Mathey Ltd., and 99.8% laboratory reagent grade RbCl was supplied by B.D.H. and the Koch-Light Company Ltd. These reagents were used without further purification and were stored in a vacuum desiccator over silica gel.

The radioactive isotopes used in this work, tritiated water, Na^{22}, Cl^{36}, and Cs^{137}, were obtained from the Radio-Chemical Centre, Amersham, Buckinghamshire.

CHAPTER 4

RESULTS AND DISCUSSION OF ISOTOPE DIFFUSION STUDIES.

4.1 Cell Calibration. The results of typical cell calibration experiments using potassium chloride solutions are given in Table (4.1). Initial and final concentrations of solution were calculated from the measured specific conductance by means of a computer programme, given in Appendix 2. Periodic re-calibration of both diffusion cells was performed at approximately six-monthly intervals. The variation in cell constant during this time was less than 0.2%. The cell constants are reported to $\pm$ 0.1%.

The results of cell calibration experiments using Na^{22} tracer in sodium chloride solutions are given in Table (4.2) together with the interpolated results of Mills[118] for the same system. Agreement is within the precision stated for Mills' data ($\pm$ 0.5%) in all cases.

4.2 Ionic Diffusion.

4.2.1 Isotopic diffusion coefficients for Cl^{36} in rubidium and caesium chloride solutions, and for Cs^{137} in caesium chloride solutions, are given in Tables (4.3), (4.4), and (4.5) respectively.

Isotope diffusion data for the remaining alkali chloride- water systems, (LiCl-, NaCl-, and KCl-H_2O), were obtained from the literature and interpolated to round-number concentrations using a least-squares curve-fit method. Coefficients of these curve-fit equations are given in Appendix 1. The diffusion data, given in Table (4.6), were obtained from several sources[41,118,173] and selected according to the general standards laid down by Mills.[118]

Some apparently obvious sources[2,35,125,180] were neglected, either because the precision was considered to be unacceptably low,[2,35,125] or because the method used was susceptible to error.[180] Results obtained by the radiometric porous frit[96] and spin-echo nmr[174,175] methods were similarly neglected on the grounds of low precision.

The L- and R-coefficient data for all the alkali chloride-water systems were obtained from the Papers of Miller,[108] Dunsmore, Jalota, and Paterson,[29] and Jalota and Paterson.[67]

Table (4.1). Typical data from a cell calibration experiment using KCl solutions.

	Cell 1		Cell 2		
cma	0.380761	0.331464	0.49919	0.42128	0.37790
cmb	0.086114	0.074551	0.04922	0.04574	0.04107
c_1	0.478475	0.416056	0.55494	0.47309	0.42450
c_2	0.000000	0.000000	0.00000	0.00000	0.00000
c_3	0.283047	0.246871	0.44344	0.36948	0.33129
c_4	0.172229	0.149101	0.09843	0.09147	0.08215
$\bar{D}_i$	1.839538	1.839452	1.84314	1.84255	1.84234
β	0.475003	0.475422	0.17253	0.17236	0.17279

Table (4.2). Results of cell calibration experiments using Na^{22} tracer in NaCl solutions.

Cell	Salt Concentration (M)	$10^5 D_{11}$	$10^5 D^*_{11}$
1	0.489	1.273	1.278
2	0.499	1.271	1.277
1	0.844	1.243	1.247
2	1.076	1.218	1.224
1	2.052	1.120	1.127
2	2.196	1.110	1.114

* Interpolated data of Mills[118] for this system.

Table (4.3). Diffusion Coefficients for Cl^{36} in RbCl solution.

Concentration (M)	$10^5 D_{22}$
0.174	1.965
0.498	1.959
1.430	1.991
2.132	2.061
2.755	2.138

Table (4.4). Diffusion Coefficients for Cl^{36} in CsCl solution.

Concentration (M)	$10^5 D_{22}$
0.103	1.974
0.305	1.962
0.489	1.964
0.902	1.945
1.566	2.023
2.799	2.173

Table (4.5). Diffusion Coefficients for Cs^{137} in CsCl solution.

Concentration (M)	$10^5 D_{11}$
0.102	1.948
0.226	1.952
0.410	1.922
0.578	1.958
0.685	1.938
0.790	1.937
0.793	1.949
0.881	1.928
1.239	1.934
1.793	1.905
2.664	1.884

Table (4.6). Ionic Diffusion Coefficients for LiCl, NaCl, and KCl solutions.

Salt	Concentration (M)	$10^5 D_{11}$	$10^5 D_{22}$
LiCl	0.0	1.029*	2.032*
	0.2	0.962	1.907
	0.5	0.946	1.817
	1.0	0.919	1.683
	2.0	0.868	1.494
	2,5	0.844	1.402
NaCl	0.0	1.333*	2.032*
	0.2	1.296	1.926
	0.5	1.272	1.861
	1.0	1.226	1.766
	2.0	1.133	1.607
	2.5	1.084	1.532
KCl	0.0	1.956*	2.032*
	0.2	1.920	1.966
	0.5	1.870	1.967
	1.0	1.850	1.956
	2.0	1.840	1.905
	2.5	1.840	1.871

* Nernst Limiting Value.

RbCl $10^5 D^0_{11} = 2.071$; $10^5 D^0_{22} = 2.032$

CsCl $10^5 D^0_{11} = 2.056$; $10^5 D^0_{22} = 2.032$

4.2.2 Interpretation of Isotopic Diffusion Coefficients.
(1) Dilute Solutions. The relationship between the diffusion coefficient of an ion and its equivalent conductance at infinite dilution, λ_i^0, was first formulated by Nernst,[127] equation (4.1).

$$10^3 D_{ii}^0 = (RT/F^2).(\lambda_i^0/|z_i|) \qquad (4.1)$$

At infinite dilution, equation (2.60) has the form

$$D_{ii}^0 = RT/C_i(R_{ii}-r_{ii'}) \qquad i=0,1,2$$

Using equation (2.19), equation (2.60) becomes:

$$D_{ii}^0 = RT/(-c_jR_{ij}-c_0R_{i0}-C_ir_{ii'}) \qquad (4.2)$$

Since $-c_jR_{ij}$ and $-C_ir_{ii'}$ represent interionic frictional interactions, these quantities vanish at infinite dilution,[29] and equation (4.2) becomes:

$$D_{ii}^0 = (RT/-c_0R_{i0})_{c_i \dashrightarrow 0} \qquad (4.3)$$

which is identical to equation (4.1), since[108]

$$\lambda_i^0 = 10^3.F^2|z_i|/-c_0R_{i0}$$

the factor 10^3 occurring from conversion of concentration units from moles/litre to moles/cm^3.

Onsager[132] and Onsager and Kim[133] discussed the diffusion of an ion present in vanishingly small amounts as a special case of multicomponent diffusion.[132] In the limiting law expression obtained by Onsager, the variation in diffusion coefficient of an ion was attributed solely to relaxation effects: long-range electrostatic interactions between an ion and its ion atmosphere. Electrophoretic effects, long-range hydrodynamic interactions between ions, were assumed to be absent, since the magnitude of such interactions depends on the concentration of the diffusing species.

The limiting law can be shown[58] to have the form:

$$D_{ii} = D^0_{ii} - (10^{-9}\lambda^0_i z_i \not{c}^2 \epsilon/3D).(4\pi/10^3 DRT)^{\frac{1}{2}}.(1-d(w_i))^{\frac{1}{2}}\sqrt{\Gamma} \qquad (4.4)$$

where $\not{c}$ is the velocity of light (cm./sec.), ϵ is the electronic charge (esu), D is the dielectric constant of the medium, and R,T, and F have their usual meaning. $d(w_i)$ is given by

$$d(w_i) = (1/\Gamma).\sum_j c_j|z_j|\lambda^0_j/(\lambda^0_j/|z_j| + \lambda^0_i/|z_i|) \qquad (4.5)$$

and Γ, the ional concentration, by

$$\Gamma = \sum_i c_i z_i^2 \qquad (4.6)$$

The limiting law has been verified experimentally by Harned and Gosting[58] and Mills[118], and is valid to concentrations of approximately 0.002M.

A simplified extension of Onsager's limiting law expression has recently been developed by Pikal[142] in terms of mobility (L_{ij}) coefficients. Pikal's expression has the form:

$$10^{12}l_{ij}/\sqrt{c_i c_j} = 0.1074\sqrt{\mu_i\mu_j}((\lambda^0_i/|z_i|)(\lambda^0_j/|z_j|)A_{ij}/(\sum\mu_i\lambda^0_i/|z_i|) - z_i z_j B_0/2).I^{\frac{1}{2}} \qquad (4.7a)$$

$$10^{12}l_{ii}/c_i = (0.1074\lambda^0_i/|z_i|) - 0.1074\left[((\lambda^0_i/|z_i|)^2.(1-\mu_i)A_{ii}/(\sum\mu_i\lambda^0_i/|z_i|)) + B_0 z_i^2\mu_i/2\right].I^{\frac{1}{2}} \qquad (4.7b)$$

where I is the total ionic strength and μ_i,μ_j are the ionic strength fractions of ionic components i,j respectively.

$$\mu_i = n_i e_i^2/\sum_{i=1}^{n} n_i e_i^2 \qquad (4.8)$$

in which e_i is the ion charge in electronic units and n_i refers to the concentration of i-type ions in (number of ions)/cm.^{3}

In equations (4.7), the terms involving A_{ij} are due to

the relaxation effect, with A_{ij} given by

$$A_{ij} = \epsilon^2 |z_i z_j| \kappa / 3DkT(2+\sqrt{2}) I^{\frac{1}{2}} \qquad (4.9)$$

where k is Boltzmann's constant (ergs/degree.mole), D is the dielectric constant of the solvent, T is the absolute temperature, ϵ is the electronic charge (esu), and κ is the reciprocal of the radius of the ion atmosphere ($cm.^{-1}$).

The electrophoretic effect is given by the terms involving B_0, where

$$B_0 = F\epsilon\kappa / 10^{-8} \not{c} 3\pi\eta_0 I^{\frac{1}{2}} \qquad (4.10)$$

in which $\not{c}$ is the velocity of light and η_0 is the viscosity of the solvent (poise).

For a system containing cation i, with tracer ion i', and anion j, under conditions of negligible tracer concentration, such that

$$C_i + c_{i'} \cong c_j = c$$

then equation (4.8) becomes, for a 1:1 electrolyte,

$$\mu_i = (n_i / n_i + n_{i'} + n_j) \cong c_i / 2c$$

and, using equation (4.7a), the isotope-isotope term $l_{ii'}/c_{i'}$ takes the form

$$10^{12} l_{ii'}/c_{i'} = (0.1074\kappa/2).((2\lambda_i^{0^2}\epsilon^2/3DkT(2+\sqrt{2})\Lambda_0) - (F\epsilon/10^{-8}\not{c}6\pi\eta_0)) \qquad (4.11)$$

A_{ij} and B_0 are independent of $I^{\frac{1}{2}}$, since κ is proportional to $I^{\frac{1}{2}}$, and so equation (4.11) above gives $l_{ii'}/c_{i'}$ (i=1,2) as a linear function of $I^{\frac{1}{2}}$.

The self-diffusion expression in terms of mobility coefficients is given by equation (2.61).

$$D_{ii} = RT((L_{ii}/C_i) - (C_i/c_i)(l_{ii'}/c_{i'}))$$

This equation reduces to the simpler form,

$$D_{ii} = RT((L_{ii}/C_i)-(1_{ii'}/c_{i'}))$$

if it is assumed that $c_{i'}$ is very small compared to c_i, and consequently $C_i = c_i$. In all but a very few cases, the most notable being the work of Longsworth,[94] this assumption is valid.

From equation (4.7), L_{ii}/C_i and $1_{ii'}/c_{i'}$ are given by

$$10^{12}L_{ii}/C_i = 0.1074\lambda_i^0-0.1074((2\lambda_i^{0^2}(1-\mu_i)A_{ii}/\Lambda_0) + B_0\mu_i/2)I^{\frac{1}{2}} \quad (4.12)$$

and

$$10^{12}1_{ii'}/c_{i'} = (0.1074/2)((2\lambda_{i'}^{0^2}A_{ii'}/\Lambda_0)-B_0/2)I^{\frac{1}{2}} \quad (4.13)$$

If chemical indistinguishability between isotopes is assumed, $A_{ii} = A_{ii'}$, $\lambda_i^0 = \lambda_{i'}^0$, and

$$D_{ii} = 10^{12}RT((L_{ii}/C_i)-(1_{ii'}/c_{i'}))$$

$$= RT(0.1074\lambda_i^0-((2\lambda_i^{0^2}(1-\mu_i)A_{ii}/\Lambda_0)+B_0\mu_i/2 + \lambda_i^{0^2}A_{ii}/\Lambda_0 - B_0/4)I^{\frac{1}{2}} \quad (4.14)$$

For a 1:1 electrolyte, $\mu_i = \frac{1}{2}$, and equation (4.14) reduces to

$$10^{-12}D_{ii} = 0.1074RT(\lambda_i^0-(2\lambda_i^{0^2}A_{ii}/\Lambda_0)I^{\frac{1}{2}}) \quad (4.15)$$

in which the terms involving B_0, the electrophoretic contribution, disappear.

Substitution of equation (4.9) in equation (4.15) gives

$$10^{-12}D_{ii} = 0.1074RT(\lambda_i^0-(2\lambda_i^{0^2}/\Lambda_0)\epsilon^2\kappa/3DkT(2+\sqrt{2})) \quad (4.16)$$

which again is a linear function of $I^{\frac{1}{2}}$, since κ is proportional to $I^{\frac{1}{2}}$.

4.2.2

(2) Concentrated Solutions. As noted previously, values of L_{ii}/C_i for all the alkali metal chloride systems are available from the literature[29,67,108] The isotope-isotope term $l_{ii'}/c_{i'}$ may be calculated using experimentally-obtained diffusion data and is in general a minor component, (<20%) of L_{ii}/C_i, becoming more important at high salt concentrations. Experimentally-observed values of $l_{ii'}/c_{i'}$ and L_{ii}/C_i are given in Table (4.7).

Since $l_{ii'}/c_{i'}$ is a minor component, an estimate of this quantity, combined with literature values of L_{ii}/C_i, may be expected to give a reasonable estimate of D_{ii}. In Table (4.8), experimentally-observed values of $l_{ii'}/c_{i'}$ are compared with those calculated by means of equation (4.11). Also shown in Table (4.8) are values of $l_{ii'}/c_{i'}$ calculated from equation (4.11) using the viscosity of the solution instead of the viscosity of the solvent.

Since limiting laws are, by definition, valid over only a relatively narrow concentration range, the concentration range involved in these Tables is too great to expect quantitative agreement. However, some degree of qualitative agreement can be seen. In addition, the limiting law correctly predicts the negative sign of $l_{ii'}/c_{i'}$, showing it to be of typical magnitude and sign of interionic coupling coefficients for like charged ions.[109] The negative sign of $l_{ii'}/c_{i'}$ is due simply to the predominance of the electrophoretic term, B_0, in equation (4.7a).

Values of D_{ii} calculated by means of equation (4.16) are compared with observed values in Table (4.9). Also given are D_{ii} obtained by a combination of calculated values of $l_{ii'}/c_{i'}$ with literature values of L_{ii}/C_i. As shown in this Table, equation (4.16) predicts ionic diffusion coefficients for all the alkali chlorides to within approximately 10% even at a concentration of 0.5M, while tending to underestimate D_{11} and overestimate D_{22}. Agreement between calculated and observed values is

(a)

Conc. (M)	LiCl		NaCl		KCl		CsCl	
	L_{11}/C_1	$-l_{11}'/c_1'$	L_{11}/C_1	$-l_{11}'/c_1'$	L_{11}/C_1	$-l_{11}'/c_1'$	L_{11}/C_1	$-l_{11}'/c_1'$
0.2	3.624	0.257	4.851	0.377	7.331	0.414	7,727	0.147
0.5	3.316	0.500	4.613	0.517	7.193	0.350	7.596	0.258
1.0	2.942	0.765	4.311	0.635	7.077	0.385	7.465	0.341
2.0	2.406	1.095	3.812	0.759	6.866	0.556	7.261	0.428
2.5	2.156	1.249	3.581	0.792	6.754	0.669	7.177	0.439

(b)

Conc. (M)	LiCl		NaCl		KCl		RbCl		CsCl	
	L_{22}/C_2	$-l_{22}'/c_2'$	L_{22}/C_2	$-l_{22}'/c_2'$	L_{22}/C_2	$-l_{22}'/c_2'$	L_{22}/C_2	$-l_{22}'/c_2'$	L_{22}/C_2	$-l_{22}'/c_2'$
0.2	7.290	0.403	7.435	0.332	7.613	0.317	7.646	0.273	7.727	0.216
0.5	6.827	0.501	7.121	0.385	7.478	0.458	7.533	0.378	7.667	0.207
1.0	6.286	0.503	6.772	0.352	7.365	0.524	7.535	0.416	7.645	0.274
2.0	5.475	0.552	6.035	0.445	7.160	0.525	7.516	0.722	7.581	0.794
2.5	5.073	0.583	5.708	0.472	7.050	0.498	7.462	1.022	7.546	1.095

Table (4.7) Experimental values of L_{ii}/C_i and l_{ii}'/c_i'. (x 10^{12})

Table (4.8) Observed and calculated values of $l_{ii'}/c_{i'}$.

(a) $-l_{11'}/c_{1'}$ ($\times 10^{12}$)

Salt	Conc. (M)	Obs.	Calculated (1)	Calculated (2)
LiCl	0.2	0.257	0.581	0.557
	0.5	0.500	0.918	0.831
	1.0	0.765	1.299	1.073
	1.5	0.940	1.596	1.200
	2.0	1.095	1.837	1.276
	2.5	1.249	2.061	1.304
NaCl	0.2	0.377	0.506	0.492
	0.5	0.517	0.799	0.748
	1.0	0.635	1.135	0.990
	1.5	0.707	1.390	1.140
	2.0	0.759	1.599	1.188
	2.5	0.792	1.794	1.231
KCl	0.2	0.414	0.328	0.328
	0.5	0.350	0.518	0.521
	1.0	0.385	0.735	0.739
	1.5	0.443	0.901	0.897
	2.0	0.556	1.036	1.027
	2.5	0.669	1.163	1.119
CsCl	0.2	0.147	0.297	0.302
	0.5	0.258	0.469	0.490
	1.0	0.341	0.664	0.719
	1.5	0.395	0.817	0.902
	2.0	0.428	0.939	1.064
	2.5	0.439	1.054	1.188

(1) From equation (4.11) using η_0.

(2) From equation (4.11) using $\eta_{soln.}$

Table (4.8) continued

(b) $-l_{22'}/c_{2'}$ ($\times 10^{12}$)

Salt	Conc. (M)	Obs.	Calculated (1)	Calculated (2)
LiCl	0.2	0.403	0.167	0.143
	0.5	0.501	0.264	0.177
	1.0	0.503	0.375	0.150
	1.5	0.497	0.459	0.063
	2.0	0.552	0.529	-0.031
	2.5	0.583	0.592	-0.164
NaCl	0.2	0.332	0.218	0.204
	0.5	0.385	0.345	0.294
	1.0	0.352	0.487	0.346
	1.5	0.419	0.597	0.332
	2.0	0.445	0.689	0.277
	2.5	0.472	0.771	0.188
KCl	0.2	0.317	0.297	0.297
	0.5	0.458	0.470	0.472
	1.0	0.524	0.665	0.670
	1.5	0.541	0.814	0.812
	2.0	0.525	0.940	0.929
	2.5	0.498	1.051	1.009
RbCl	0.2	0.273	0.308	0.315
	0.5	0.378	0.488	0.508
	1.0	0.416	0.690	0.737
	1.5	0.518	0.846	0.914
	2.0	0.722	0.975	1.065
	2.5	1.022	1.092	1.179
CsCl	0.2	0.216	0.307	0.312
	0.5	0.207	0.485	0.506
	1.0	0.274	0.687	0.741
	1.5	0.501	0.843	0.930
	2.0	0.794	0.971	1.096
	2.5	1.095	1.089	1.224

(1),(2) calculated as for $-l_{11'}/c_{1'}$.

Table (4.9) Observed and calculated values for D_{ii} (i=1,2).

(a) $10^5 D_{11}$

Salt	Conc. (M)	Obs.	Calculated (1)	Calculated (2)	Calculated (3)
LiCl	0.2	0.962	0.959	1.042	1.036
	0.5	0.946	0.918	1.050	1.028
	1.0	0.919	0.872	1.051	0.995
	1.5	0.893	0.835	1.056	0.957
	2.0	0.868	0.806	1.052	0.913
	2.5	0.844	0.779	1.045	0.858
NaCl	0.2	1.296	1.226	1.328	1.324
	0.5	1.272	1.163	1.342	1.329
	1.0	1.226	1.092	1.349	1.314
	1.5	1.180	1.037	1.349	1.287
	2.0	1.133	0.992	1.341	1.239
	2.5	1.084	0.950	1.332	1.193
KCl	0.2	1.92	1.76	1.90	1.90
	0.5	1.87	1.65	1.91	1.91
	1.0	1.85	1.52	1.94	1.94
	1.5	1.84	1.42	1.95	1.95
	2.0	1.84	1.34	1.96	1.96
	2.5	1.84	1.26	1.96	1.95
CsCl	0.2	1.952	1.845	1.989	1.990
	0.5	1.947	1.723	1.999	2.004
	1.0	1.935	1.584	2.015	2.029
	1.5	1.921	1.476	2.026	2.047
	2.0	1.906	1.387	2.033	2.064
	2.5	1.888	1.307	2.040	2.074

(1) From equation (4.16).

(2) From equation (4.11), using ζ_o and literature L_{11}/C_1.

(3) From equation (4.11), using ζ_{sdm} and literature L_{11}/C_1.

Table (4.9) continued

(b) $10^5 D_{22}$

Salt	Conc. (M)	Obs.	Calculated (1)	(2)	(3)
LiCl	0.2	1.907	2.005	1.849	1.842
	0.5	1.817	1.989	1.758	1.736
	1.0	1.683	1.970	1.651	1.595
	1.5	1.580	1.957	1.571	1.472
	2.0	1.494	1.945	1.488	1.350
	2.5	1.402	1.935	1.404	1.217
NaCl	0.2	1.926	2.007	1.897	1.894
	0.5	1.861	1.993	1.851	1.838
	1.0	1,766	1.976	1.799	1.764
	1.5	1.683	1.964	1.727	1.661
	2.0	1.607	1.953	1.667	1.565
	2.5	1.532	1.944	1.606	1.462
KCl	0.2	1.966	2.011	1.961	1.961
	0.5	1.967	1.999	1.970	1.971
	1.0	1.956	1.985	1.991	1.992
	1.5	1.935	1.974	2.003	2.002
	2.0	1.905	1.965	2.008	2.005
	2.5	1.871	1.958	2.008	1.998
RbCl	0.2	1.963	2.012	1.972	1.973
	0.5	1.961	2.000	1.989	1.993
	1.0	1.971	1.986	2.039	2.051
	1.5	1.998	1.976	2.079	2.096
	2.0	2.042	1.967	2.105	2.127
	2.5	2.103	1.960	2.120	2.142
CsCl	0.2	1.969	2.012	1.992	1.993
	0.5	1.952	2.000	2.021	2.026
	1.0	1.963	1.986	2.066	2.079
	1.5	2.011	1.976	2.096	2.117
	2.0	2.076	1.967	2.120	2.151
	2.5	2.142	1.959	2.141	2.174

(1),(2),(3) calculated as before.

particularly good for D_{22}, though calculated values of both D_{11} and D_{22} are up to 35% in error at higher concentrations.

Frictional coefficient representation.

Equation (2.60) represents the diffusion coefficient of an ion in terms of $C_i R_{ii}$, the sum of all frictional interaction between component i and all the other species in the system,[29] and $C_i r_{ii'}$, the frictional interaction between component i' and those i per unit volume.

Experimentally-observed values of $C_i R_{ii}$ and $C_i r_{ii'}$ are given in Table (4.10). $C_i r_{ii'}$ is positive, which is the usual situation between species which have mutual repulsion, as shown by Miller[109] and also by Pikal[142] in his equations for R_{ij} in multicomponent solutions.

Both $C_i R_{ii}$ and $C_i r_{ii'}$ increase with increasing concentration, as expected, due to the increase in the number of ions per unit volume. However, expanding $C_i R_{ii}$ according to equation (2.19),

$$C_i R_{ii} = -C_j R_{ij} - c_0 R_{i0} \qquad (4.17)$$

then D_{ii} may be represented by

$$10^5 D_{ii} = 10^3 RT/(-C_j R_{ij} - c_0 R_{i0} - C_i r_{ii'}).$$

$C_j R_{ij}$ and $C_i r_{ii'}$ both represent interionic friction, and both contain relaxation and electrophoretic terms. Since these quantities are of opposite sign, an empirical equation for D_{ii} is obtained if it is assumed that $C_j R_{ij}$ and $C_i r_{ii'}$ approximately cancel, giving equation (4.18)

$$D_{ii} \cong RT/-c_0 R_{i0} \qquad (4.18)$$

This equation is exact at infinite dilution, when

$$C_j R_{ij} = C_i r_{ii'} = 0$$

(a)

Conc. (M)	LiCl		NaCl		KCl		CsCl	
	C_1R_{11}	C_1r_{11}'	C_1R_{11}	C_1r_{11}'	C_1R_{11}	C_1r_{11}'	C_1R_{11}	C_1r_{11}'
0.2	2.799	0.222	2.088	0.175	1.380	0.089	1.311	0.041
0.5	3.083	0.463	2.215	0.266	1.419	0.093	1.355	0.082
1.0	3.492	0.795	2.388	0.366	1.454	0.114	1.393	0.112
2.0	4.282	1.426	2.722	0.534	1.514	0.167	1.451	0.150
2.5	4.769	1.832	2.904	0.617	1.545	0.198	1.477	0.164

(b)

Conc. (M)	LiCl		NaCl		KCl		RbCl		CsCl	
	C_2R_{22}	C_2r_{22}'	C_2R_{22}	C_2r_{22}'	C_2R_{22}	C_2r_{22}'	C_2R_{22}	C_2r_{22}'	C_2R_{22}	C_2r_{22}'
0.2	1.392	0.092	1.363	0.076	1.329	0.068	1.319	0.056	1.322	0.063
0.5	1.497	0.133	1.435	0.103	1.365	0.105	1.355	0.091	1.342	0.072
1.0	1.634	0.161	1.532	0.128	1.397	0.130	1.370	0.112	1.360	0.097
2.0	1.882	0.223	1.719	0.176	1.452	0.151	1.393	0.179	1.389	0.195
2.5	2.027	0.259	1.822	0.204	1.480	0.155	1.411	0.232	1.405	0.248

Table (4.10) Experimental values of C_iR_{ii} and C_ir_{ii}'. (x 10^{-11})

Observed values of $C_j r_{ij}$ and $C_i r_{ii}$, are given in Table (4.11).

Since Pikal[142] has shown that $-c_0R_{i0}$ does not contain relaxation terms, then equation (4.18) describes the variation of D_{ii} with concentration solely in terms of ion-solvent interactions.

Values of D_{ii} calculated using equation (4.18) are compared to those observed in Table (4.12). Qualitative agreement between calculated and observed data is good, within 10-15% in most cases, indicating that it is a reasonable approximation to ascribe the variation in D_{ii} with concentration to purely ion-water (electrophoretic) interaction.

If equation (4.18) is re-written in the form:

$$D_{ii} \cong RT/(-c_0R^o_{i0}+\Delta(-c_0R_{i0})) \qquad (4.19)$$

where $-c_0R^o_{i0}$ is the value of $-c_0R_{i0}$ at infinite dilution, then $\Delta(-c_0R_{i0})$ represents the variation of $-c_0R^o_{i0}$ with solution concentration. Since $-c_0R_{i0}$ is a measure of the friction between ion i and those water molecules per unit volume, the behaviour of $\Delta(-c_0R_{i0})$ with increasing concentration of solution will give an indication of the solvent environment around ion i. Figures 4.1 and 4.2 show the variation of $\Delta(-c_0R_{i0})$ with concentration. $\Delta(-c_0R_{i0})$ increases rapidly with increasing concentration for solutions of LiCl and NaCl, and remains approximately zero with increasing concentration for solutions of KCl, RbCl, and CsCl.

This may be rationalised in terms of water structure[160] and the effects of ions on that structure. The solvent order-producing ions Li^+ and Na^+ increase the water structure[51] whereas the ions K^+, Rb^+, and Cs^+ decrease the water structure and enhance the mobilities of other species. Cl^- ion is order-destroying, but in the case of LiCl and NaCl solutions, the order-producing nature of the cation exerts the dominating influence.

Conc. (M)	LiCl			NaCl			KCl		
	C_1r_{11}'	$-C_2R_{12}$	C_2r_{22}'	C_1r_{11}'	$-C_2R_{12}$	C_2r_{22}'	C_1r_{11}'	$-C_2R_{12}$	C_2r_{22}'
0.2	0.222	0.236	0.092	0.175	0.191	0.076	0.089	0.147	0.068
0.5	0.463	0.316	0.133	0.266	0.261	0.103	0.093	0.197	0.105
1.0	0.795	0.388	0.161	0.366	0.324	0.128	0.114	0.240	0.130
2.0	1.426	0.486	0.223	0.534	0.411	0.176	0.167	0.288	0.151
2.5	1.832	0.515	0.259	0.617	0.450	0.204	0.198	0.308	0.155

Conc. (M)	RbCl			CsCl		
	C_1r_{11}'	$-C_2R_{12}$	C_2r_{22}'	C_1r_{11}'	$-C_2R_{12}$	C_2r_{22}'
0.2	-	0.142	0.056	0.041	0.160	0.063
0.5	-	0.193	0.091	0.082	0.226	0.072
1.0	-	0.242	0.112	0.112	0.270	0.097
2.0	-	0.298	0.179	0.150	0.319	0.196
2.5	-	0.320	0.232	0.164	0.342	0.248

Table (4.11) Observed values of C_jR_{ij} and C_ir_{ii}'. (x 10^{-11})

	Conc. (M)	LiCl D_{obs}	LiCl D_{calc}	NaCl D_{obs}	NaCl D_{calc}	KCl D_{obs}	KCl D_{calc}	CsCl D_{obs}	CsCl D_{calc}
(a)	0.2	0.96	0.97	1.30	1.31	1.92	2.01	1.95	2.15
	0.5	0.95	0.90	1.27	1.27	1.87	2.03	1.95	2.20
10^5D_{11}	1.0	0.92	0.80	1.23	1.20	1.85	2.04	1.94	2.21
	2.0	0.87	0.65	1.13	1.07	1.84	2.02	1.91	2.19
	2.5	0.84	0.58	1.08	1.01	1.84	2.00	1.89	2.19

	Conc. (M)	LiCl D_{obs}	LiCl D_{calc}	NaCl D_{obs}	NaCl D_{calc}	KCl D_{obs}	KCl D_{calc}	RbCl D_{obs}	RbCl D_{calc}	CsCl D_{obs}	CsCl D_{calc}
(b)	0.2	1.91	2.14	1.93	2.12	1.97	2.09	1.97	2.14	1.96	2.09
	0.5	1.82	2.10	1.86	2.11	1.97	2.12	1.95	2.22	1.96	2.13
10^5D_{22}	1.0	1.68	1.99	1.77	2.05	1.96	2.14	1.96	2.27	1.97	2.20
	2.0	1.49	1.78	1.61	1.90	1.91	2.13	2.08	2.32	2.04	2.26
	2.5	1.40	1.64	1.53	1.81	1.87	2.12	2.10	2.27	2.14	2.33

Table (4.12). Observed and calculated values of 10^5D_{ii}.

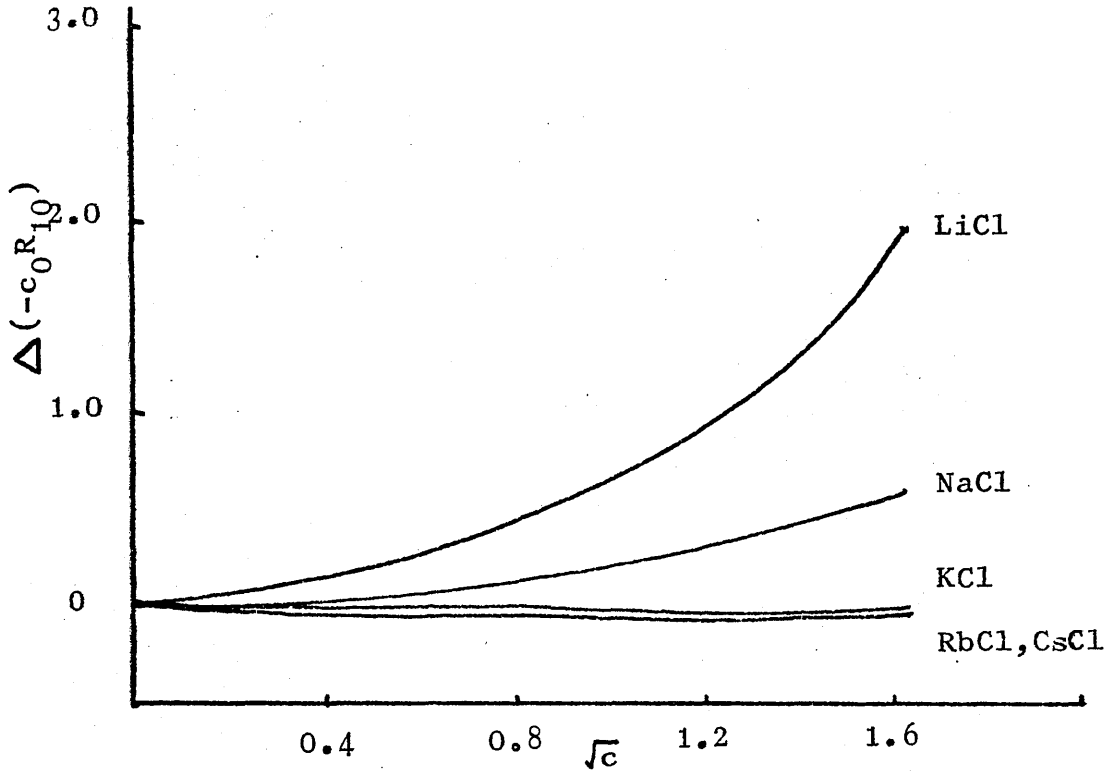


Figure 4.1 $\Delta(-c_0R_{10})$ vs $\sqrt{c}$ for the alkali chlorides.

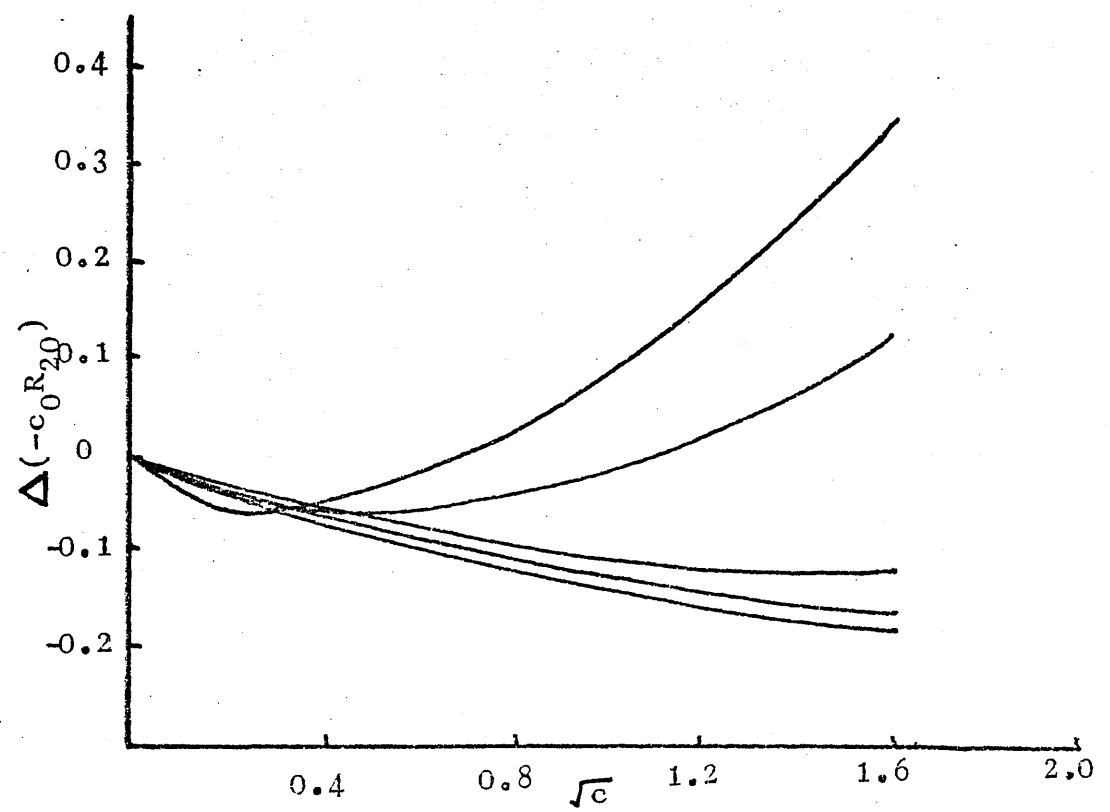


Figure 4.2 $\Delta(-c_0R_{20})$ vs $\sqrt{c}$ for the alkali chlorides.

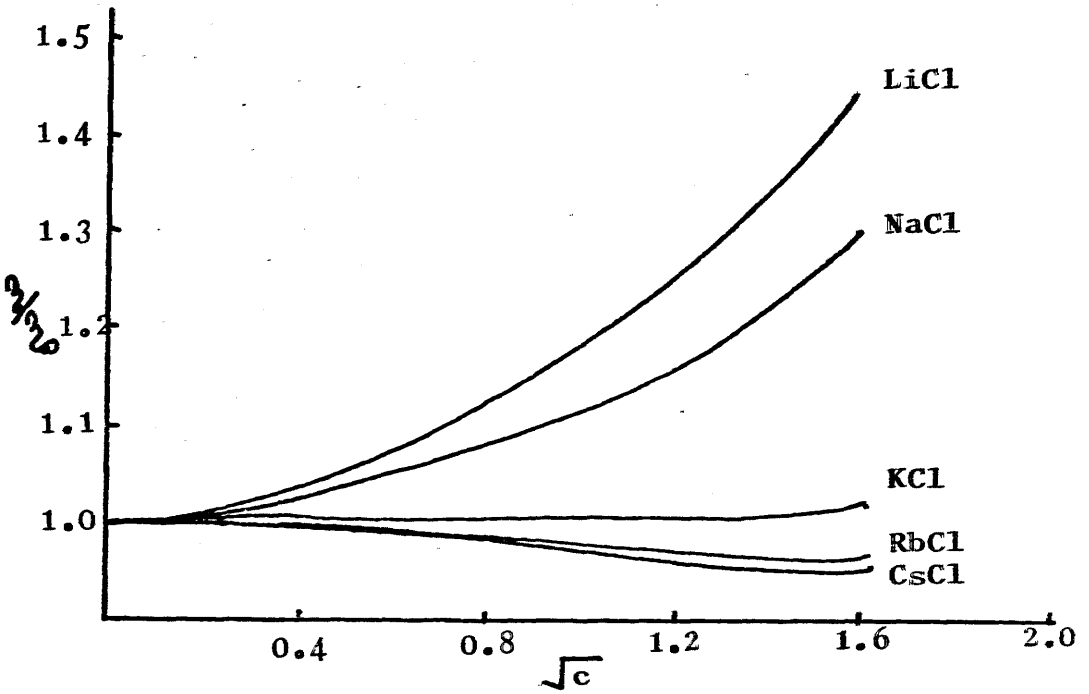


Figure 4.3 η/η_0 vs $\sqrt{c}$ for the alkali chlorides.

The variation in relative viscosity, η/η_0, with concentration is shown in Figure 4.3 for alkali metal chloride solutions. The similarity between Figure 4.3 and Figures 4.1 and 4.2 is apparent. However, according to Curie's theorem,[49] vector flows cannot result from tensor forces, so there can be no direct macroscopic connection between viscosity, a tensor, and diffusion, a vector. At the microscopic level, however, the local viscosity of the fluid surrounding an ion may differ markedly from the viscosity of the bulk solution, thus any theoretical consideration of diffusion which takes into account the bulk viscosity can at best be semi-empirical.

4.3 Water Diffusion.

Tracer diffusion of isotopically-labelled water in electrolyte solutions has been studied extensively by a number of workers.[14,15,74,100,103,182,185] Nevertheless, large discrepancies exist in the literature between different workers as to the value of the tracer diffusion coefficient at infinite dilution. Unlike diffusion of ionic species, in which the limiting value of the diffusion coefficient may be computed by the Nernst equation, there exists no comparable theory or practical method for calculating this quantity. A review of reported values, with estimated errors, is presented in Table (4.13). It should be noted that the tracer diffusion coefficients differ markedly depending on the tracer isotope used, so that

$$D_{HTO} \neq D_{HDO} \neq D_{H_2O}$$

where the subscript refers to the tracer species used, and D_{H2O} is the true self-diffusion coefficient of water. Mass effects are important in the tracer diffusion of water, though they may be considered virtually negligible in the tracer diffusion of ions.[143] However, mass effects are smaller than might be expected from an

Table (4.13). Tracer diffusion coefficients of water at 25°C.

Reference	Tracer	Method	$10^5 D_{00}$
136	HDO	D.C.	2.43 ±0.01
181	HDO	o.e.c.	2.34 ±0.08
47	HDO	D.C.	2.04 ±0.10
178	HDO	D.C.	2.13 ±0.03
93	HDO	Inter.	2.272 ±0.004
178	HDO	o.e.c.	2.13 ±0.04
26	HDO	C.C.	2.25 ±0.02
92	HDO	Inter.	2.261 ±0.02
135	HDO	D.C.	2.64 ±0.10
161	-	NMR	2.13 ±0.15
172	-	NMR	2.51 ±0.03
17	-	NMR	2.5 ±0.3
28	-	NMR	2.35 ±0.12
103	-	NMR	2.44 ±0.12
104	-	NMR	2.45 ±0.12
40	-	NMR	2.23 ±0.10
3	H_2O^{18}	o.e.c.	2.57 ±0.3
181	H_2O^{18}	o.e.c.	2.66 ±0.12
183	H_2O^{18}	o.e.c.	2.57 ±0.02
26	HTO	C.C.	2.25 ±0.02
74	HTO	c.m.c.	2.22 ±0.04
23	HTO	D.C.	2.64 ±0.13
181	HTO	o.e.c.	2.44 ±0.06
145	HTO	o.e.c.	2.59 ±0.03
121	HTO	D.C.	2.236 ±0.01
14,15	HTO	o.e.c.	2.24 ±0.04
This work	HTO	D.C.	2.19 ±0.04

D.C. --- Diffusion Cell

o.e.c. --- Open-ended Capillary

C.C. --- Capillary Cell

c.m.c. --- Continuously-Monitored Capillary

Inter. --- Interferometry

inverse square-root dependence such as that found in dilute gases,[105]

$$D/D_i = (M_i/M)^{\frac{1}{2}}$$

where i is the isotopically labelled molecule.

The most accurate value for the tracer diffusion coefficient of HDO in pure water is that obtained by Longsworth[93,94] using a Rayleigh interferometric technique. The accuracy of this method is at least within $\pm$ 0.2%, and so the diffusion coefficient of HDO in water may be taken to be $2.272.10^{-5}$ $cm.^2/sec.$

Of the other determinations of the diffusion coefficient of HDO in water, only those of Wang et al.[181] and Devell[26] agree with the value of Longsworth within the stated limits of error. The values of Partington, Hudson, and Bagnall[136] and Orr and Butler[135] are considerably higher, and those of Wang[178] and Graupner and Winter,[47] considerably lower than Longsworth's value. The reasons for the discrepancies are not clear, though the value of Orr and Butler[135] may be disregarded as their method did not involve stirring of the diffusing solutions, leading to erroneous results.

For water labelled with O^{18}, the results appear to be higher than expected from purely mass considerations, though the determinations of Wang et al.,[181] Adamson and Irani[3], and more recently of Wang[183], all agree within the stated limits of error.

For tritiated water, the values of Jones, Rowlands, and Monk,[74] Devell[26], Brun[14,15], and Mills[121], agree, within the stated limits of error, on a value of approximately $2.23.10^{-5}$ $cm.^2/sec.$ The data of Cuddleback, Koeller, and Drickamer,[23] Wang, Robinson, and Edelman[181], and Pruppacher[145] are all somewhat higher. It should be noted, however, that Wang et al.[181] used a turbulent stirring method, which tends to give high results,[118] and Cuddleback et al.[23] used Orr and Butler's[135] data to calibrate their apparatus.

The value for D_{HTO} of $2.19.10^{-5}$ $cm.^2/sec.$ obtained

in this laboratory is the mean of four determinations using two different diffusion cells. These results are shown in Table (4.14). Though somewhat lower, this value agrees with the generally accepted value[120] of $2.23.10^{-5}$ cm.^{2}/sec. within the limits of experimental error ($\pm$ 2%).

Studies of the diffusion of water in alkali chloride-water solutions at 25° C have been confined to relatively few workers, chiefly Brun [14,15] and Wang [182], both of whom used the capillary method. The results of Wang are somewhat higher than those of Brun, possibly for reasons discussed earlier, and so more reliance must be placed on the latter data. These results are shown in Table (4.15) ; results ob tained in this work are shown in Table (4.16) and graphically in Figure 4.4.

Agreement between the two sets of results is generally within the combined experimental errors ($\pm$ 4%) for all the systems, though correlation between the two sets of data becomes poorer in solutions of LiCl more concentrated than $\sim$1.2M and solutions of NaCl more concentrated than $\sim$2M.

Diffusion data measured in this laboratory were interpolated to round-number concentrations, and the isotope-isotope frictional coefficient was calculated for each system at each concentration using equation (2.61).

$$10^5 D_{00} = RT/c_0(R_{00}-r_{00'})$$

where the subscript 0 denotes the bulk solvent and 0' the isotopically-labelled form of solvent.

Numerical values of the quantity $-c_0r_{00'}$ and the relative magnitude of c_0R_{00} to $-c_0r_{00'}$ are given in Table (4.17). The isotope-isotope friction term, $-c_0r_{00'}$, is much greater than c_0R_{00}, the sum of the frictional coefficients between water and ions:

$$c_0R_{00} = -c_0R_{10} - c_0R_{20}$$

Table (4.14) Diffusion coefficients of water in pure water.

Cell	$10^5 D_{00}$
1	2.198
2	2.186
1	2.174
2	2.210

Table (4.15) Data of Brun[14,15] for the diffusion coefficients of water.

Salt	Concentration (M)	$10^5 D_{00}$
LiCl	0.608	1.98
	1.166	1.83
	2.000	1.66
	2.856	1.51
	4.040	1.31
NaCl	1.000	2.03
	1.500	1.96
	2.000	1.88
	2.500	1.78
	3.000	1.69
KCl	0.500	2.37
	1.000	2.36
	2.000	2.28
	2.500	2.23
	3.000	2.19
RbCl	0.500	2.24
	1.000	2.23
	1.500	2.34
	1.823	2.39
	2.500	2.35
	3.062	2.35
CsCl	0.053	2.20
	0.500	2.25
	0.792	2.26
	1.103	2.28
	2.103	2.35
	3.496	2.30

Table (4.16) Diffusion coefficients of water.

Salt	Concentration (M)	$10^5 D_{00}$
LiCl	0.256	2.143
	0.561	2.036
	1.198	1.902
	1.711	1.835
	2.499	1.666
NaCl	0.208	2.188
	0.328	2.175
	0.500	2.164
	0.801	2.130
	1.063	2.083
	1.508	2.021
	1.926	1.969
	2.385	1.881
	2.862	1.779
KCl	0.206	2.231
	0.351	2.241
	0.470	2.262
	0.720	2.279
	1.271	2.287
	1.891	2.283
	2.532	2.252
	2.823	2.234
RbCl	0.279	2.259
	0.508	2.297
	0.768	2.299
	0.994	2.328
	1.532	2.362
	2.719	2.384
CsCl	0.176	2.241
	0.690	2.306
	1.249	2.357
	2.414	2.378

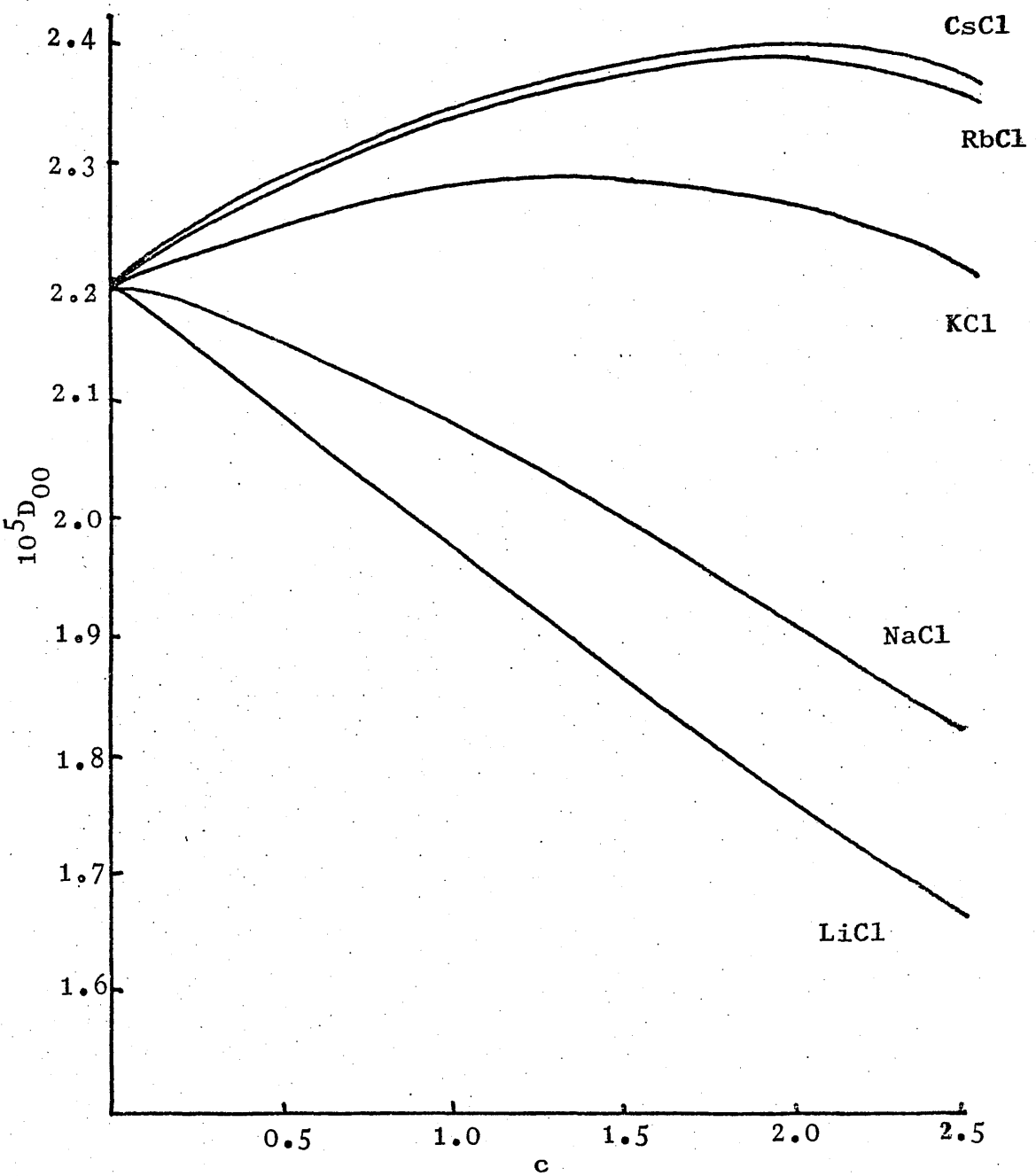


Figure 4.4 $10^5 D_{00}$ vs c for the alkali chlorides.

Conc. (M)	$-c_0R_{00}'$	R	$-c_0R_{00}'$	R	$-c_0R_{00}'$	R	$-c_0R_{00}'$	R	$-c_0R_{00}'$	R
0.0	1.131	0.0	1.131	0.0	1.131	0.0	1.131	0.0	1.131	0.0
0.2	1.144	1.22	1.121	0.98	1.101	0.82	1.091	0.82	1.096	0.73
0.5	1.162	3.10	1.120	2.59	1.076	2.04	1.064	1.97	1.064	1.97
1.0	1.187	6.74	1.120	5.36	1.042	4.22	1.023	4.11	1.019	4.12
2.0	1.216	16.04	1.137	11.96	0.994	9.26	0.957	8.99	0.953	9.13
2.5	1.211	22.59	1.154	15.75	0.981	12.00	0.915	11.99	0.932	11.91

$R = 10^2 c_0R_{00}/-c_0R_{00}'$

Table (4.17). $-c_0R_{00}'$ ($\times 10^{-11}$) for the alkali chlorides.

Furthermore, $-c_0r_{00'}$ does not vanish at infinite dilution, but tends to a limiting value. Figures 4.5 and 4.6 show the variation of c_0R_{00} and $-c_0r_{00'}$ as a function both of salt and of concentration of salt.

c_0R_{00} always increases with increasing concentration, regardless of the salt solution, the increase being more pronounced for solutions of LiCl and NaCl than for solutions of KCl, RbCl, and CsCl. This increase is a natural consequence of the increase in ion-water friction as concentration increases. In the absence of changes in $-c_0r_{00'}$, therefore, the increasing contribution of ion-water friction would tend to decrease the diffusion coefficient of water.

However, $-c_0r_{00'}$ does vary both with concentration and with salt, in general increasing in solutions of LiCl and NaCl and decreasing in solutions of KCl, RbCl, and CsCl. Since $c_0r_{00'}$ is negative, the quantity $c_0(R_{00}-r_{00'})$ is positive, and will increase or decrease with increasing concentration according to the behaviour of $-c_0r_{00'}$.

In solutions of LiCl and NaCl, $-c_0r_{00'}$ increases overall, passing through a maximum for LiCl and a shallow minimum for NaCl. According to Gurney's [51] concepts of the state of the solvent in the vicinity of an ion, Li^+ and Na^+ ions are solvent order-producing and enhance the structure of the solvent, thus increasing ion-solvent friction. Li^+ ion exerts the greater effect on water structure due to its higher charge density.

In solutions of KCl, RbCl, and CsCl, $-c_0r_{00'}$ decreases regularly, since K^+,Rb^+,Cs^+ and Cl^- ions are all solvent order-destroying and tend to loosen the water structure and decrease ion-solvent friction. The effect of the alkali metal cations on the structure of water in concentrated solutions has the observed order [66]

$$Li^+ > Na^+ > K^+ > Rb^+ \cong Cs^+$$

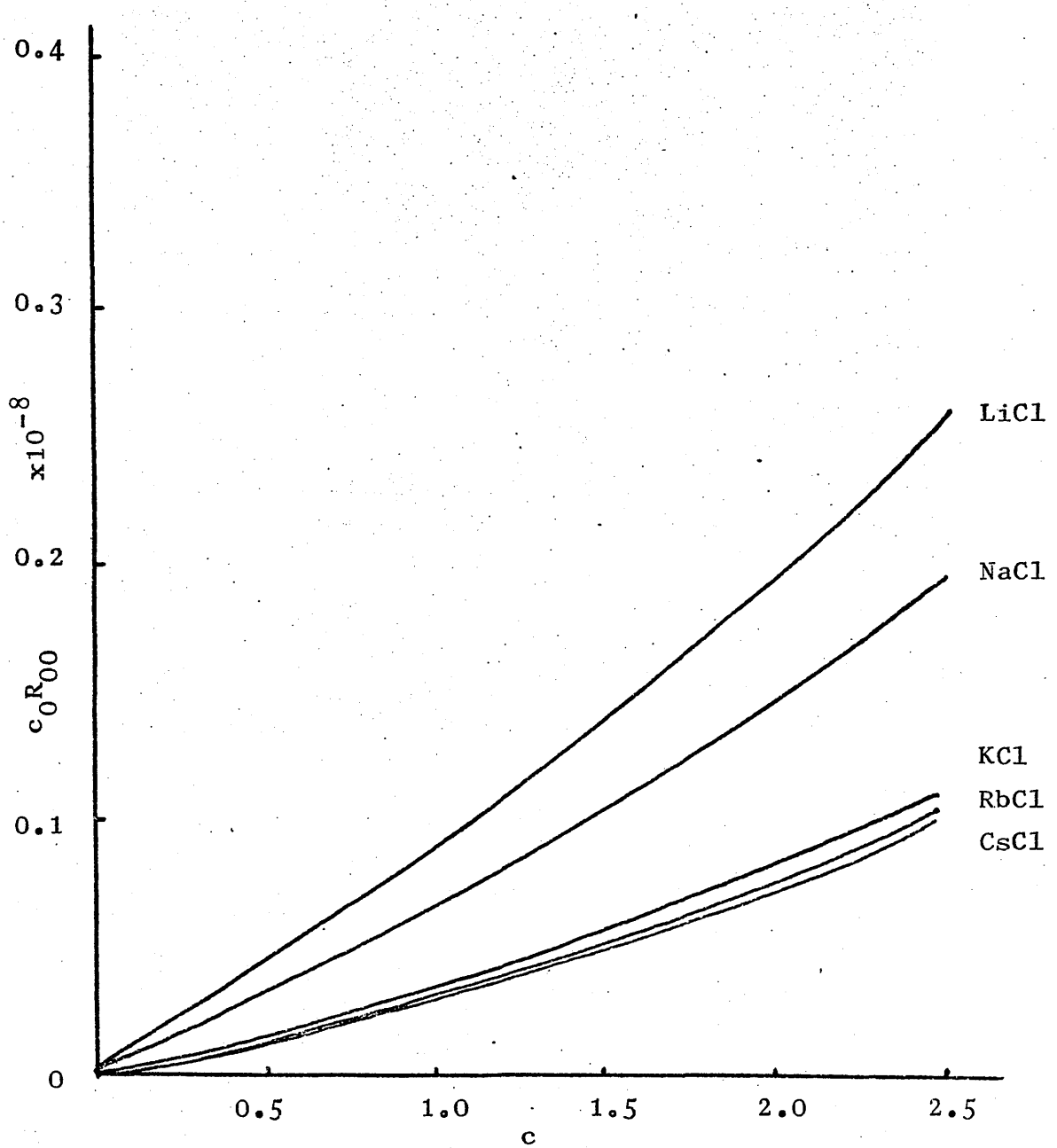


Figure 4.5 c_0R_{00} vs c for the alkali chlorides.

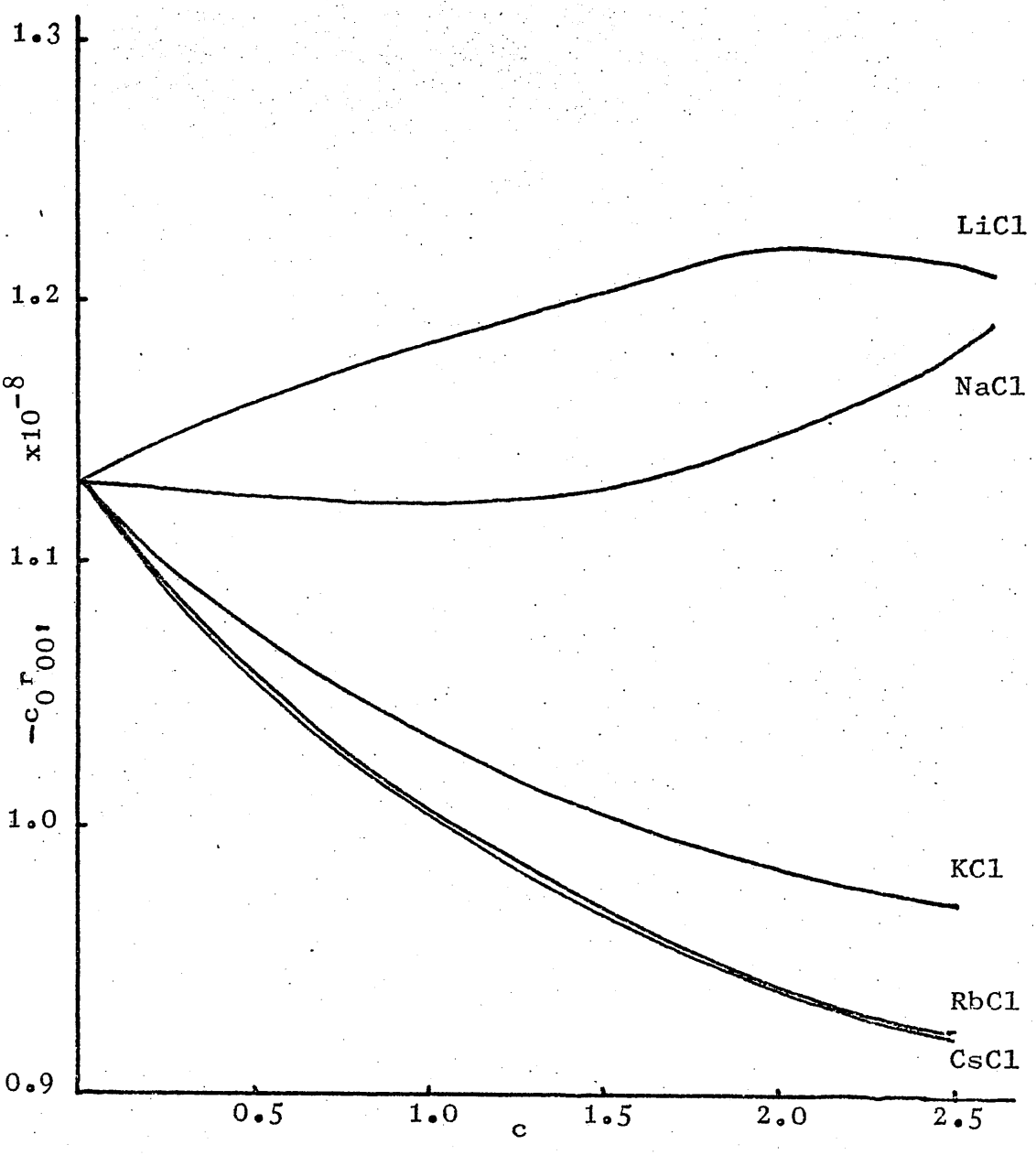


Figure 4.6 $-c_0 r_{00'}$ vs c for the alkali chlorides.

Thus the trends in variation of the diffusion coefficient of water as a function of salt may be rationalised in terms of the effect of the alkali metal cation on the water structure.

The relationship between the bulk viscosity of a solution and the effect on water structure of its constituent solute has long been known.[22,52,75] The relative viscosity, η/η_o, is given by the equation of Jones and Dole[70], equation (4.20).

$$\eta/\eta_o = \eta_{rel} = 1 + Ac^{\frac{1}{2}} + Bc \qquad (4.20)$$

in which the sign of the B-coefficient is strongly correlated with the effect on water structure of the ions. Negative B-coefficients indicate a structure-breaking effect, positive B-coefficients a structure-producing effect. In Figures 4.7a-e, η/η_o and D^o/D, the relative isotopic diffusion coefficient of water, are plotted against $c^{\frac{1}{2}}$. In all cases, the viscosity curve is close to the D^o/D curve, over a wide concentration range, though again there can be no direct macroscopic connection between the two quantities.

Though semi-empirical equations relating viscosity to diffusion may be obtained, any eventual theoretical treatment of the problem must involve the use of more fundamental quantities influencing the parallel processes of diffusion and viscous flow.

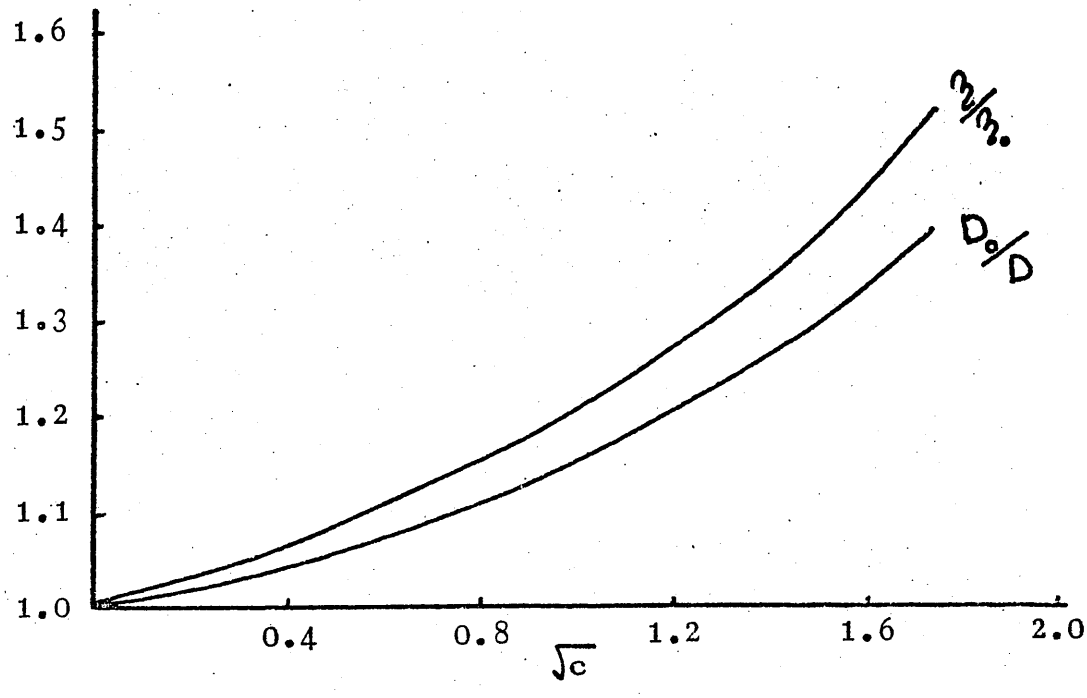


Figure 4.7a η/η_0 or D_0/D vs $\sqrt{c}$ for LiCl.

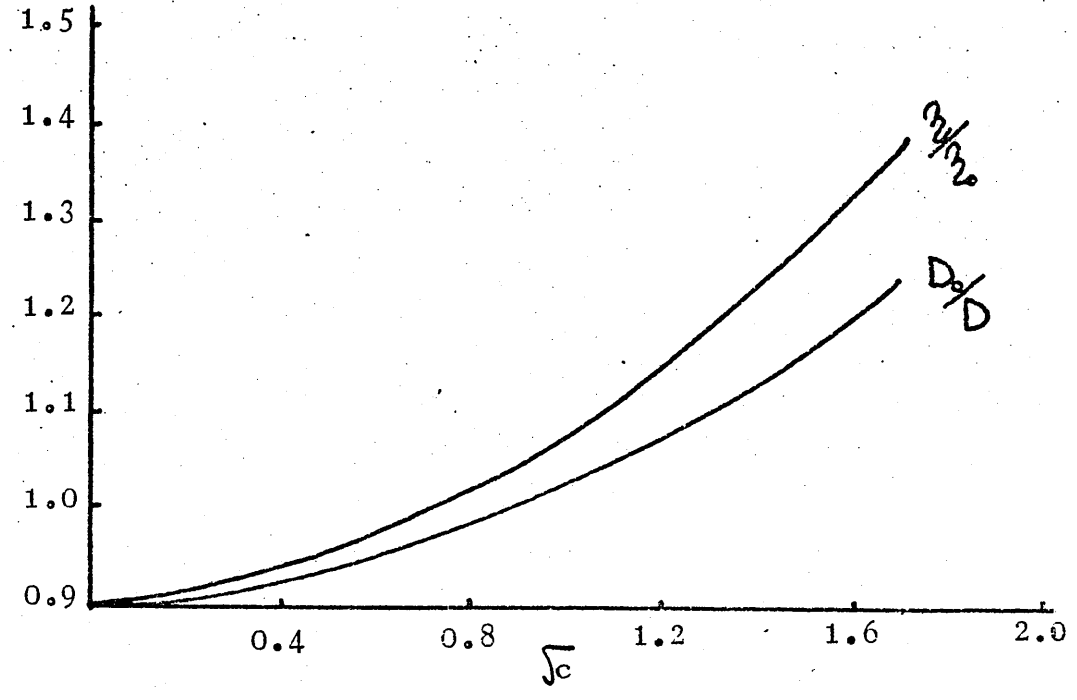


Figure 4.7b η/η_0 or D_0/D vs $\sqrt{c}$ for NaCl.

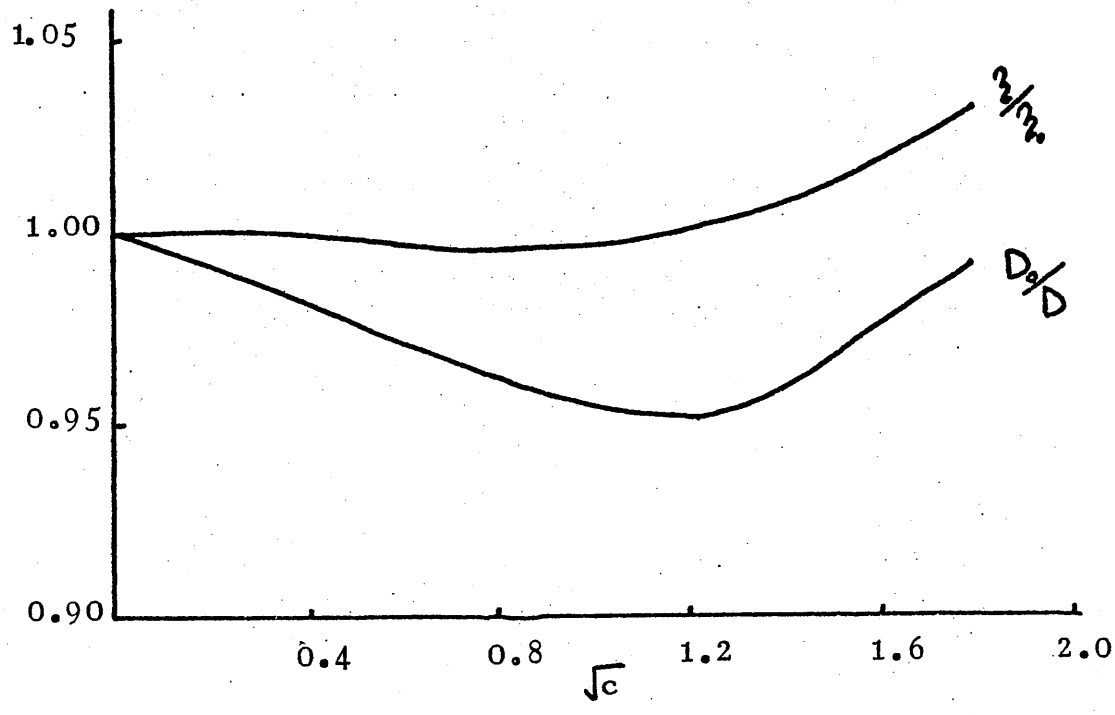


Figure 4.7c η/η_0 or D_0/D vs $\sqrt{c}$ for KCl.

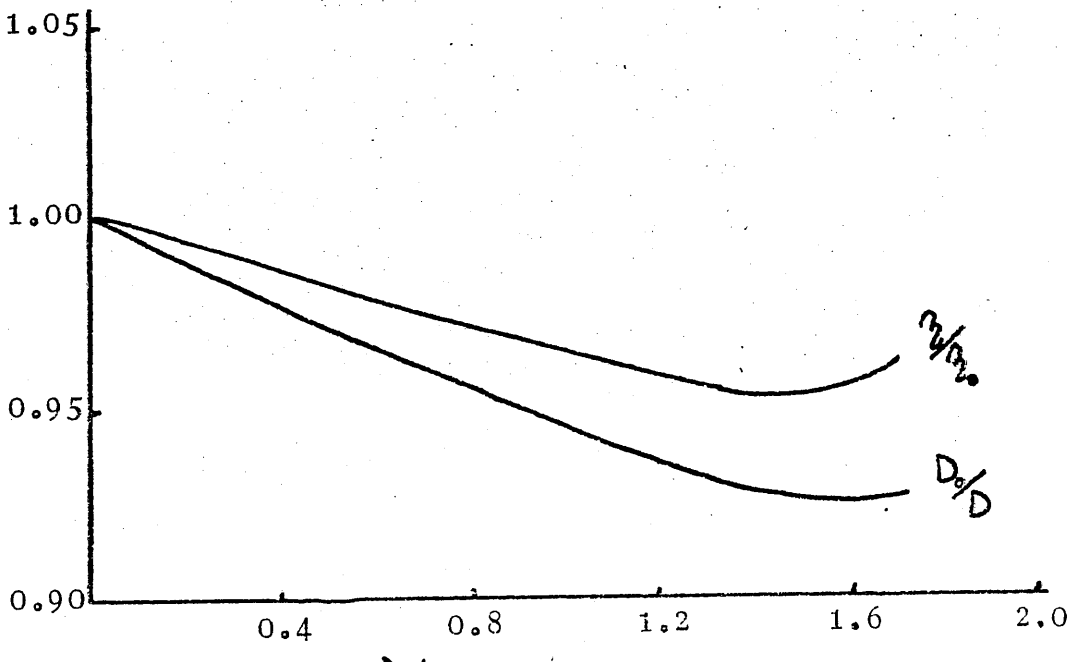


Figure 4.7d η/η_0 or D_0/D vs $\sqrt{c}$ for RbCl.

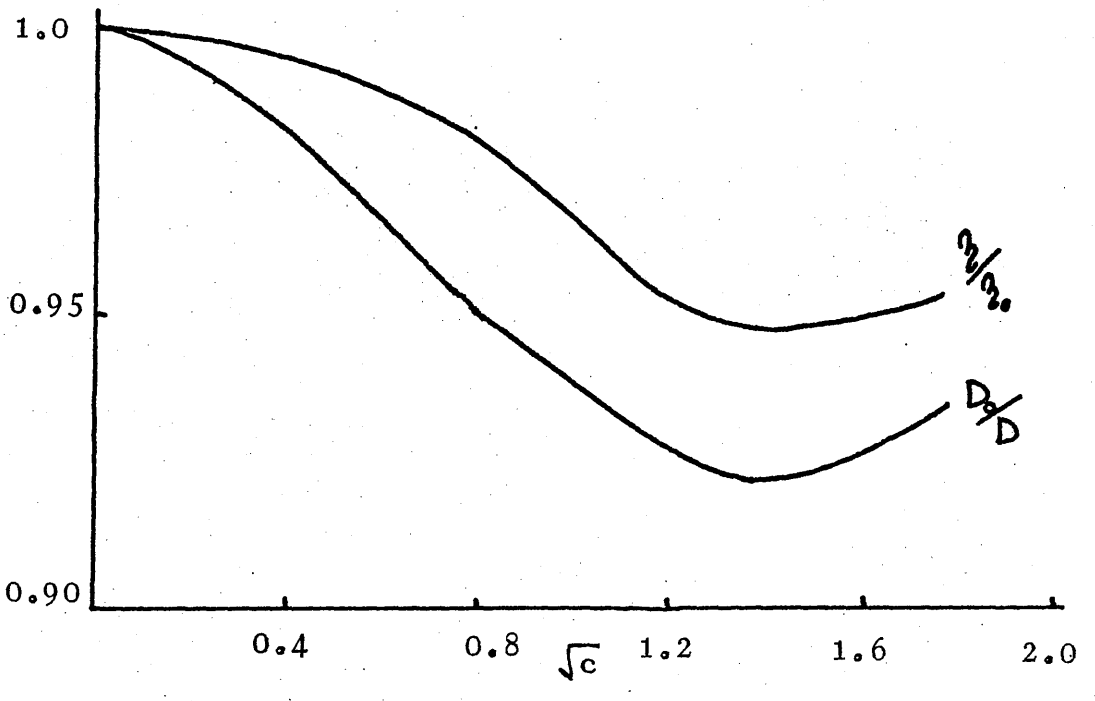


Figure 4.7e η/η_0 or D_0/D vs $\sqrt{c}$ for CsCl.

CHAPTER 5

MEASUREMENT OF THE TRANSPORT PARAMETERS FOR THE SYSTEM CdI_2-H_2O

5.1 Introduction.

The system cadmium iodide-water was chosen for study principally because of its known self-complexing behaviour, as part of a more general study of complexing salts, including $ZnCl_2$ and $CdCl_2$.

The system itself has been fairly extensively studied over the last fifty years. Transport numbers (at 18^oC) were determined as long ago as 1901,[12] and more recently by Sahay.[159] Conductance has been measured by Rabinowitsch, and van Rysselberghe et al.[158] Diffusion coefficients were measured by McBain, van Rysselberghe, and Squance,[101] using a diaphragm cell method, and more recently by Garland, Tong, and Stockmayer,[37] using a porous frit technique. In addition, activity coefficient data are available from a number of sources.[7,39,50,156]

However, much of the data from different sources differ significantly, particularly in the case of diffusion coefficients, and to a lesser extent conductance. Also, those data which are available are limited in range, particularly so in the case of transport numbers.

Measurement of the quantities t_i, D, and Λ was therefore undertaken primarily for the purpose of comparison with existing data, and secondly to extend these data in order that a complete irreversible thermodynamic analysis be made.

ADDENDUM

Cadmium iodide of high nominal purity was obtained commercially from Merck Ltd. The stoichiometric ratios of Cd : I in solution were 1 : 2, within the limits of analysis ($\pm$ 0.05% for each component). Solutions were prepared using doubly-distilled conductivity water.

5.2 Measurement of Salt Diffusion Coefficients. Methods applicable to the measurement of isotopic diffusion coefficients have been discussed previously in Chapter 3. An outline of the major methods available for the study of bulk salt diffusion is given below. Such methods have been discussed in detail in several reviews.[11,38,68,89,152]

5.2.1 The Diaphragm Cell. This method has been described in considerable detail in Chapter 3.

With careful experimental technique, diffusion coefficients to an accuracy of ±0.2% may be obtained.[29,67] This method has recently also been applied to the study of multicomponent diffusion.

5.2.2 Optical Methods. Optical methods are in general the most accurate available at the present time. All are based on the solution of Fick's Second Law,

$$\partial c/\partial t = D.\partial^2 c/\partial x^2 \qquad (5.1)$$

for free diffusion from an initially sharp boundary between two solutions of different concentration in an effectively infinite column of solution. Initially, therefore, there is a sharp discontinuity in refractive index, and as diffusion proceeds this discontinuity becomes an increasingly broad region of gradual change of refractive index, which can be studied by suitable optical arrangements.

Most optical methods use interferometric techniques to observe the refractive index gradient, and it is the interferometric method of Gouy which has received the most widespread use.

The phenomenon by which an interference pattern is produced when a beam of collimated light is passed through a cell in which diffusion is occurring in a vertical direction was first reported by Gouy.[46] The pattern produced consists of a number of horizontal bands. The intensity of these bands is greatest, and the spacing between them least, near the initial boundary between the diffusing solutions.

A complete theoretical description of the phenomenon has been given by Gosting and Onsager,[45] and also by Coulson et al.,[21] and Kegeles and Gosting.[77] The method is restricted to concentrations large enough to give a 'reasonable' number of bands or fringes in the interference pattern; at least 30 are desirable for 0.1% accuracy.

For the same reason, the concentration difference between the two solutions must be small, of the order of 0.05M, and this minimises the density gradient acting to stabilise the column of solution against convection.

The Gouy method is one of the most exact of those available at present for measuring diffusion coefficients, and several investigators, notably Gosting et al.[43] and Longsworth,[91] have developed the method to an accuracy of 0.2%. Recent applications have been to the study of multicomponent diffusion.[24,36]

Other optical methods include the Longsworth[88] 'schlieren scanning' method and the 'diagonal schlieren' method of Philpot,[138] which are important in the study of colloids. A method applicable to the study of dilute solutions has been developed by Bryngdahl.[16] This method involves birefringent interferences, with the effect of amplifying the refractive index differences in the diffusing solution, and has been applied to the study of very dilute solutions, in which the Gouy and other interferometric methods are impractical.

5.2.3 The Conductimetric Method. This method may be termed a 'restricted diffusion' method, in contrast to the free diffusion methods in which the length of the diffusing column is assumed to be effectively infinite.

The conductimetric method was developed by Harned and coworkers[56,57] for dilute solutions. The method consists essentially of diffusion in a cell of finite length, and the decay of a concentration gradient with time is monitored by measuring the conductivity at two points in the cell. Conductivity is measured by means of two pairs of electrodes set in opposite walls of the cell at heights $l/6$ and $5l/6$, where l is the height of the cell.

The solution of equation (4.1) for a diffusing column of

height 1, with boundary conditions:

$$\partial c/\partial x = 0 \text{ at } x = 0 \text{ and } x = \ell$$

has the form of a Fourier series.

$$c = c_0 + \sum_{n=1}^{\infty} A_n . \exp(-n^2\pi^2 Dt/\ell^2) . \cos(n\pi x/1) \qquad (5.2)$$

where D is the diffusion coefficient in $cm.^2/sec.$, t is time in seconds, x is the distance in cm. from the bottom of the cell, ℓ is the length of the cell in cm., c is concentration, and c_0 and the A_n's are constants.

The difference in concentration between planes $x = \ell/6$ and $x = 5\ell/6$ is:

$$c_{1/6} - c_{5/6} = \sum_{n=1}^{\infty} A_n . \exp(-n^2\pi^2 Dt/\ell^2) \left[\cos n\pi/6 - \cos 5n\pi/6\right]$$

which reduces to

$$c_{1/6} - c_{5/6} = 2A_1 . \exp(-\pi^2 Dt/\ell^2) . \cos\pi/6 - 2A_5 . \exp(-25\pi^2 Dt/\ell^2) . \cos\pi/6 + \ldots\ldots\ldots \qquad (5.3)$$

Due to the factor 25 in the exponent in the second term of equation (5.3), the series converges rapidly even at small values of time. At sufficiently large times, the second term may be neglected, and a plot of $\ln(c_{1/6} - c_{5/6})$ versus time will be linear, with slope $-D\pi^2/\ell^2$.

The same exponential form will hold for any property which is proportional to concentration.

The conductimetric method can only be used for solutions in which conductance is a linear function of concentration, and so is most useful for the study of solutions more dilute than 0.05M. Elaborate precautions must be taken to avoid thermal and vibrational disturbances, but despite these difficulties, data accurate to 0.1% have been obtained.[57]

5.3 The Study of Diffusion using Rayleigh Interferometry.

For most electrolytes, the refractive index is very nearly a linear function of concentration over small concentration ranges, and this approximation becomes increasingly better as the concentration range diminishes.

Thus the principle of Harned's conductimetric method can be extended to concentrated solutions by the study of changes in refractive index rather than changes in conductivity.

Changes in concentration are monitored by measuring changes in refractive index by means of a suitable optical system.

The system used was devised by Philpot and Cook;[139] the principle was also discovered independently by Svensson.[170] Application of the method has been due to Longsworth,[92] Moore and Opperman,[122] and Chapman.[19]

The type of cell used is a Tiselius cell, the standard apparatus for electrophoresis studies, which is directly applicable to the study of restricted diffusion. The cell is shown schematically in Figure 5.1.

The height of the centre section is approximately 8.5 cm., each channel or limb having a cross-section of 3 mm. by 24 mm. The top and bottom sections contact the centre section on lightly greased ground glass flanges. The centre section may be isolated (Figure 5.2a), leaving an enclosed column of solution of exactly the height of the centre section.

If a concentration gradient is introduced into the cell, then the diffusing column may be isolated and observed optically. The rate of change of concentration difference between points in the cell $\ell/6$ and $5\ell/6$ may be determined from the change in the interference pattern, and the diffusion coefficient may be calculated according to equation (5.3), neglecting second and higher terms.

5.3.1 Theoretical Aspects. The principle of Rayleigh interferometry is the ability of two coherent light beams to interfere constructively or destructively, depending on the phase difference of their waves. In Figure 5.3, two parallel beams of light are in phase at points A and B. At point M on screen S, the beams may be either in phase or out of phase depending

Figure 5.1 Schematic representation of the diffusion cell.

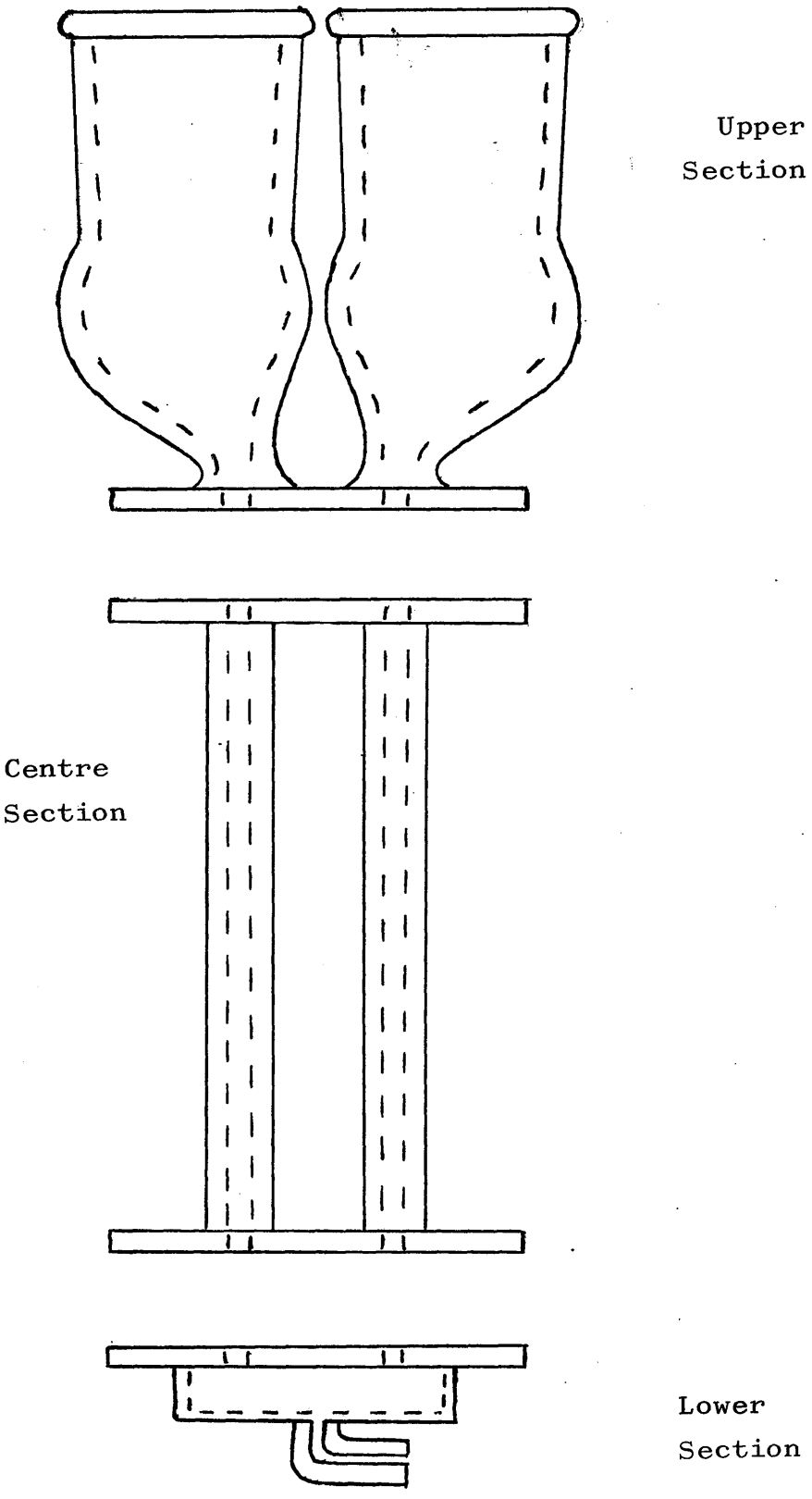
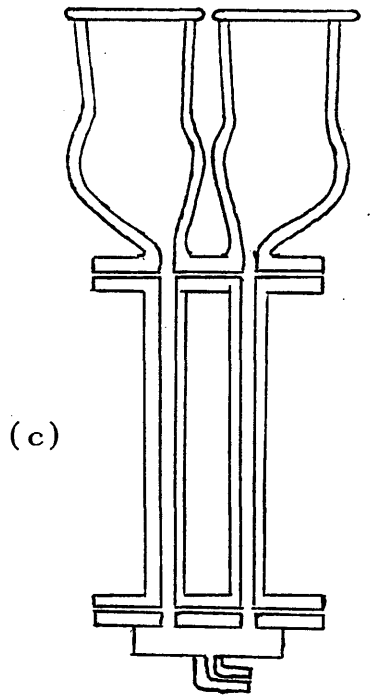
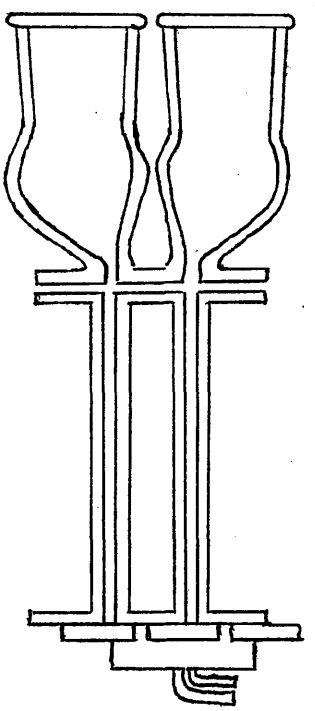


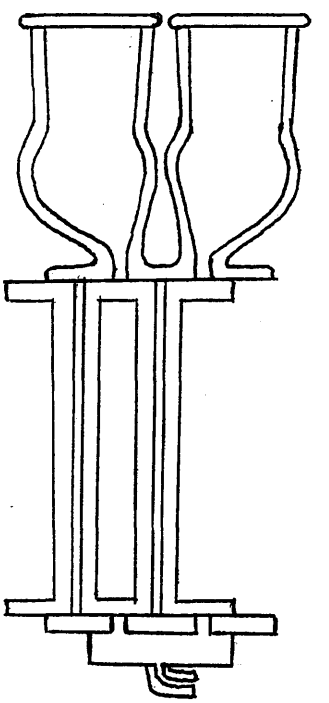
Figure 5.2 Relative positions of the sections of the cell during the filling procedure.



(c)



(b)



(a)

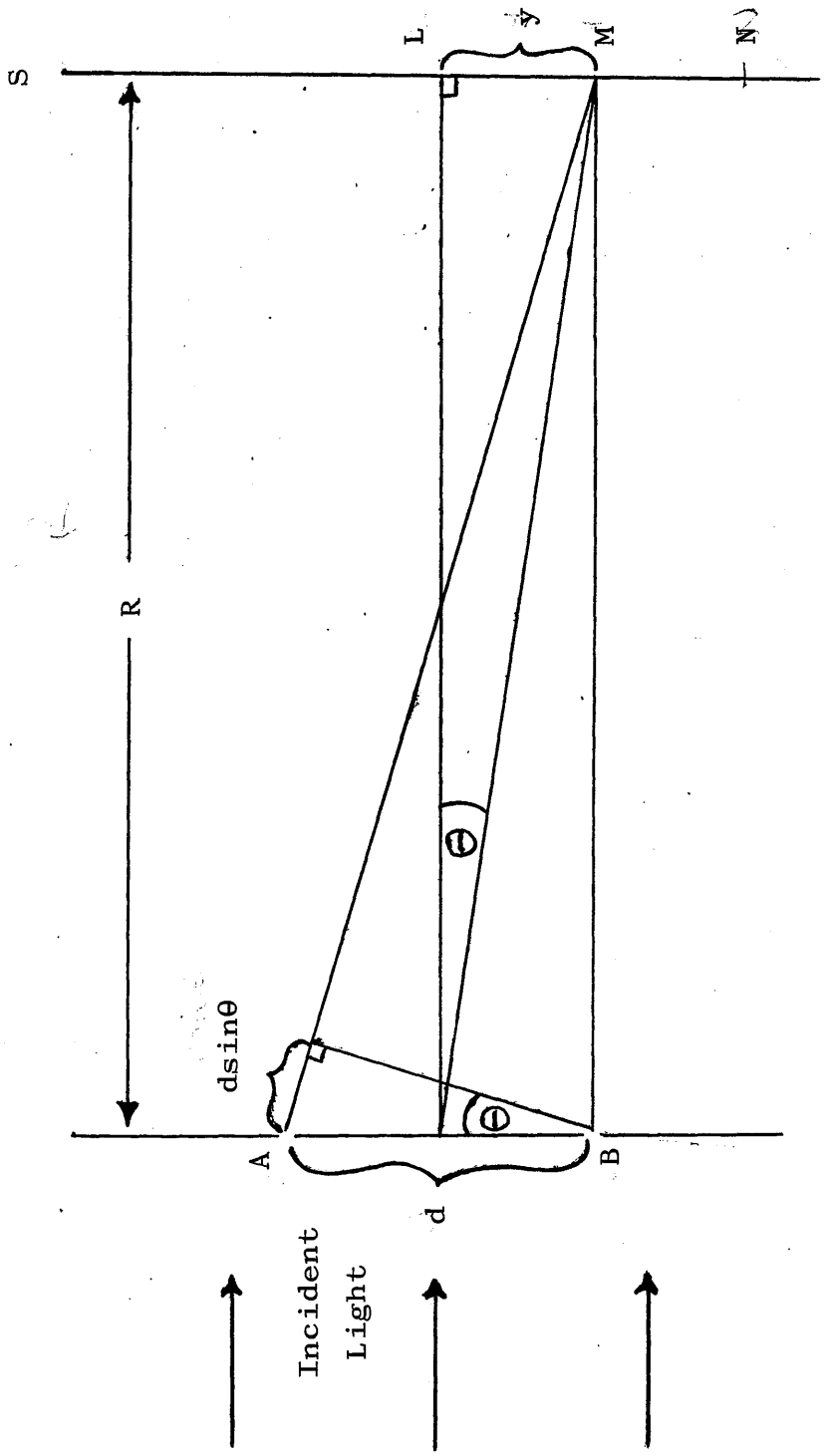


Figure 5.3 Origin of the interference fringes.

on the distance each has travelled.

If distance LM = y and AB = d, and the distance from slits to screen be R, then the path difference of the beams is $d\sin\theta$, where

$$\theta = \tan^{-1}(y/R)$$

When $d\sin\theta$ is an integral number of wavelengths, then the beams are in phase and the intensity is a maximum.

$$\text{i.e., when} \quad d\sin\theta = m\lambda \qquad m = 1,2,\ldots,n$$

As distance LM increases to LN, the beams become progressively out of phase until, at the point $d\sin\theta = (m+1/2)\lambda$, the intensity is a minimum. At the point LN = 2y, the beams are again in phase, $d\sin\theta = (m+1)\lambda$, and the intensity is again a maximum. Thus a system of alternating light and dark bands or fringes appears on the screen.

If, however, the beams are out of phase at A and B, then the positions of intensity maxima on the screen are shifted according to the relation:

$$d\sin\theta_m = m\lambda - \delta\lambda$$

where δ is the fraction of a wave by which the beams at A and B are out of phase, and θ_m are the angles at which intensity maxima appear.

Two beams of light can be out of phase by virtue of the fact that they have traversed different optical path lengths, and $\delta\lambda$ represents this path difference.

Since the optical path length in a medium is the product of actual distance, r, and the refractive index, μ, of the medium, then a path difference can arise from a difference in μ as well as from a difference in r.

If different media, of thicknesses r_A and r_B and refractive indices μ_A and μ_B, are placed behind slits A and B, then

$$\delta\lambda = \mu_A r_A - \mu_B r_B$$

If $r_A = r_B$, then $\delta\lambda = r(\mu_A - \mu_B)$, and the condition for inter-

ference becomes

$$d\sin\theta_m = m\lambda - r(\mu_A - \mu_B)$$

As the quantity $(\mu_A - \mu_B)$ changes, the value of θ_m, and therefore the positions of the interference fringes, must also change. A difference in refractive index difference between media at slits A and B causes a shift of the entire interference pattern.

At point M in Figure 5.3 there is an intensity maximum when $\mu_A = \mu_B$. If μ_B is constant and μ_A varies, then at point M

$$r\Delta\mu_A = \Delta m\lambda \qquad (5.4)$$

The order of the interference, m, depends upon the change in μ_A, and only when $\Delta\mu_A$ is such that Δm is an integer will an intensity maximum appear at M.

Equation (5.4) is the condition applicable when a Rayleigh interferometer is used to determine a concentration change. A change in refractive index $\Delta\mu_A$ in a sample solution is identified by the number of fringe shifts, Δm.

If two cells, one containing a one-dimensional concentration gradient, and one which serves as a comparison path, (in the experimental situation merely the medium of the thermostat bath), are placed adjacent to the slits in Figure 5.4, and the cylindrical lens K inserted as indicated, then this lens serves to focus the vertical extent of the images of the cells on the screen without distorting the interference patterns which exist on every horizontal line. The screen in the experimental situation was a photographic plate.

Since the vertical dimensions of the interference pattern correspond to the vertical dimensions of the sample cell, then a gradual change in refractive index of solution in the cell can be related to a gradual shifting or bending of the fringes along a vertical trace. Thus a pattern of curved fringes the same shape as the concentration profile is obtained.

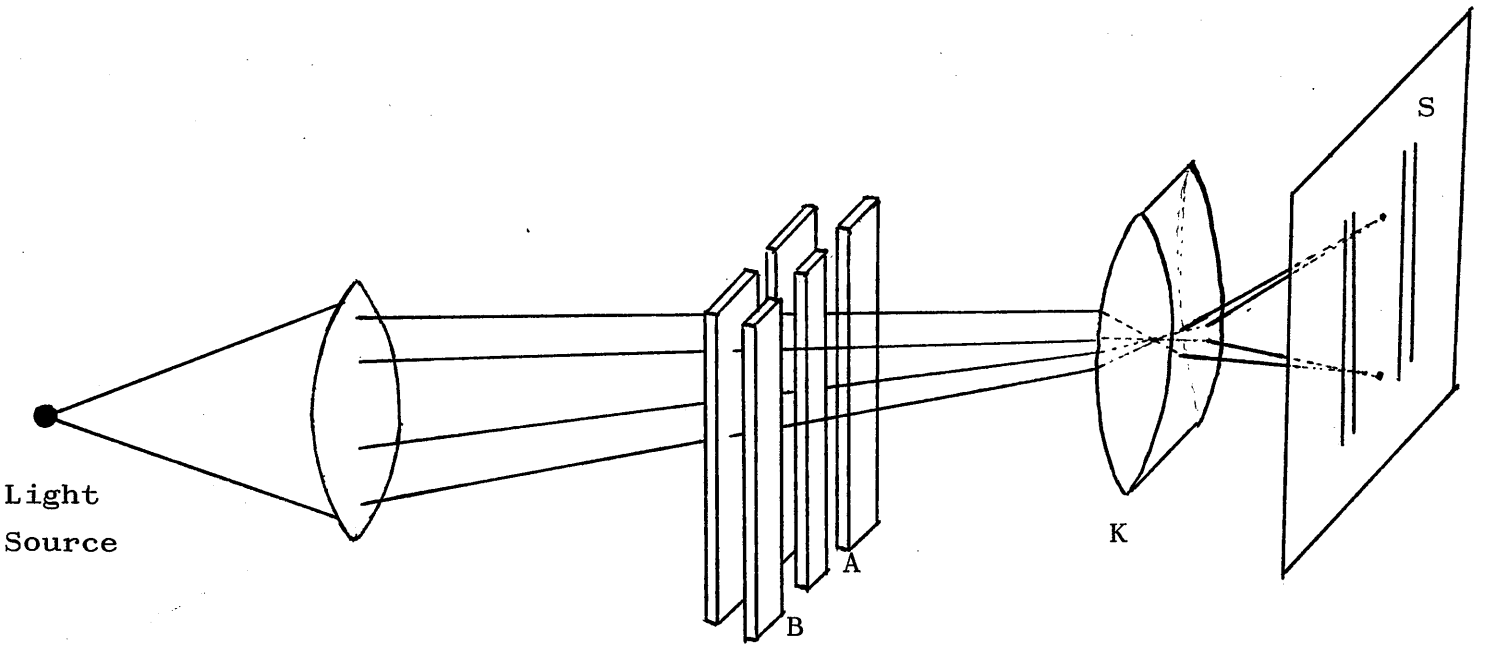


Figure 5.4 Simplified diagram of a Rayleigh Interferometer.

5.3.2 The Optical System. The optical system used is shown schematically in Figure 5.5. A choice is offered between schlieren and Rayleigh optics, the latter being used for diffusion measurements.

The apparatus and cells were obtained commercially from Measuring and Scientific Equipment Ltd. The exact dimensions of the cells were determined by Barr and Stroud Ltd.;lengths were reported to ± 0.0003 cm.

Fine lines were inscribed across the faces of each limb of the cell at points exactly one-sixth and five-sixths of the overall length. These lines appeared as faint but discernible markings across the photographs of fringe patterns, and served as a reliable frame of reference both for the orientation of the fringes and for the vertical position of the cell.

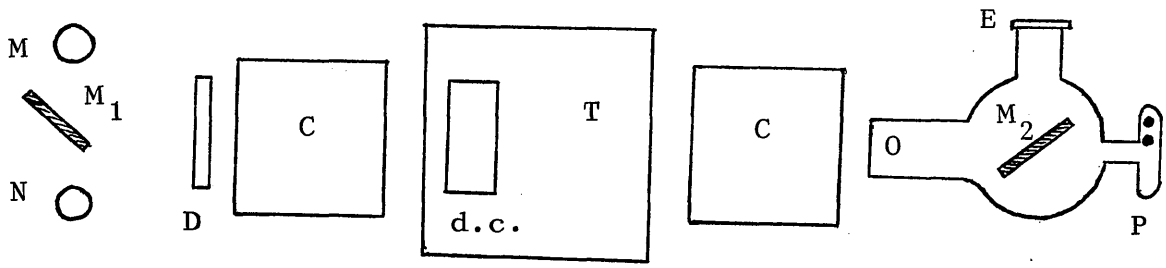
5.3.3 The Cell Assembly. As shown in Figure 5.1, the cell consisted of three parts. The centre part of the cell consisted of two limbs, rectangular parallelipipeds in shape, between flat ground-glass flanges. On isolation of this part from the rest of the cell, the height of the column of diffusing liquid is the overall length of this piece, therefore accurate knowledge of this quantity is essential.

The lower section was simply a flat ground-glass flange with a small box on the bottom which closed a U between the two limbs of the centre section through holes in the flange. A small capillary tube led from the box, to which a glass reservoir was fitted by means of a short length of Teflon tubing.

The top section consisted of a flat ground-glass flange with two slits through which the channels of the centre section were extended.

Prior to assembly, any possible traces of grease on the optical surfaces of the centre section were removed by thorough rinsing with Analar grade cyclohexane. All parts of the cell were then washed for at least 24 hours in a solution of Decon 75, a mild detergent. They were then rinsed thoroughly with tap water followed by distilled water, and dried using

Figure 5.5 Schematic diagram of the optical system.



M	Monochromatic light source.
N	Visible light source.
M_1,M_2	Adjustable mirrors.
D	Diffraction grating.
C	Collimator lens systems.
T	Constant temperature bath.
d.c.	Diffusion cell assembly.
O	Optical system.
P	Camera.

Analar grade acetone.

MSE silicone grease was used to seal and lubricate all ground-glass surfaces between sections, and the assembled cell was clamped into the cell holder by means of the spring clips as shown in Figure 5.6. All experimental solutions were filtered using a Millipore filter unit and degassed for 20-25 minutes before use.

The cell holder incorporated a piston arrangement which allowed both the top and bottom sections to be displaced from the centre section by depressing plungers at the top of the holder. This permitted isolation of the centre section at the outer surfaces of its flanges by the opposing flange surfaces.

Glass reservoir E in Figure 5.6 was filled with the most concentrated solution. All channels of the cell were aligned, Figure 5.2c, and solution from the reservoir was allowed to flow slowly into the bottom part of the cell, ensuring no air bubbles remained trapped. When solution had just entered the centre section, the bottom section was isolated, Figure 5.2b, and the small amount of solution remaining in each limb was removed. Each limb was then rinsed several times with distilled water and with dilute solution.

Finally, each limb and corresponding part of the top section was filled with the appropriate solution and the cell holder was placed in a constant-temperature bath maintained at 25°C $\pm$0.005 by means of a coiled glass mercury-toluene regulator. Circulation of the bath fluid was achieved by electric stirrers mounted on vibration-absorbing pads in two corners of the bath.

The difference in refractive index between the bath fluid and the solutions in the cell was normally such that a poorly-defined interference pattern was obtained. Longsworth [91] resolved this problem by placing pieces of flat glass in the reference beam. It was found to be more convenient to alter the refractive index of the bath fluid by adding a sufficient quantity of ethylene glycol to the bath water to match approximately the refractive index of the sample solutions. The effect of this procedure is illustrated in Figures 5.7a and b.

Concentration differences of the order of 0.04M were em-

Figure 5.6 Cell holder for the diffusion cell.

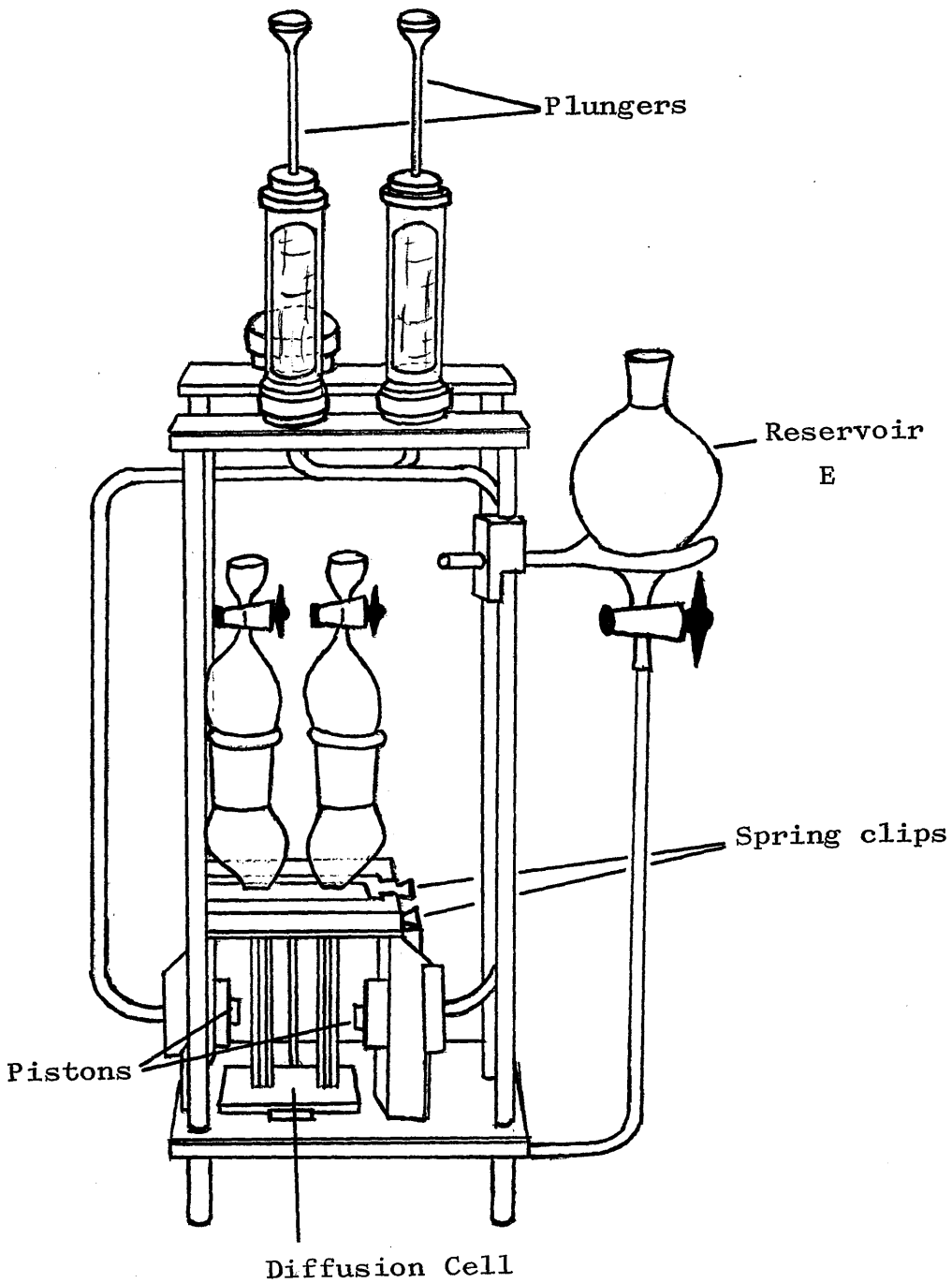
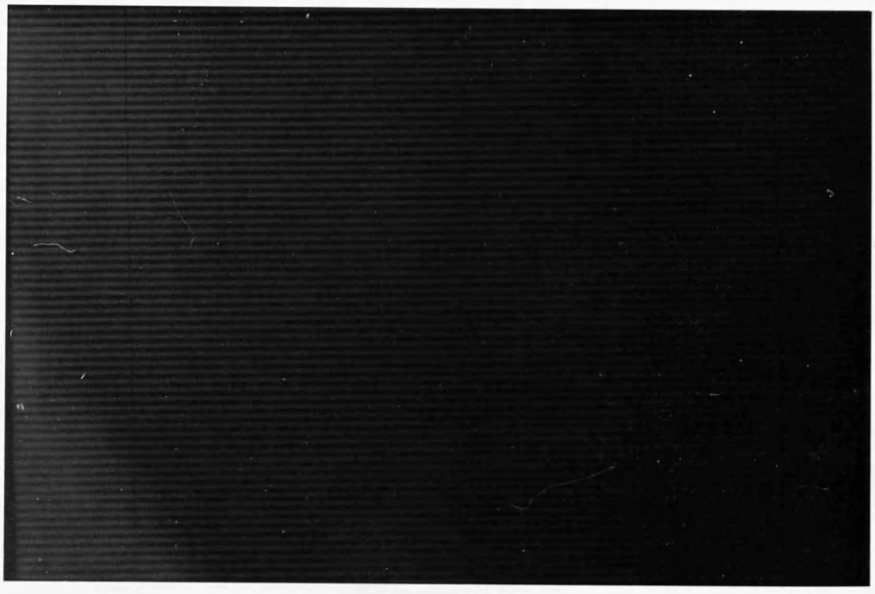
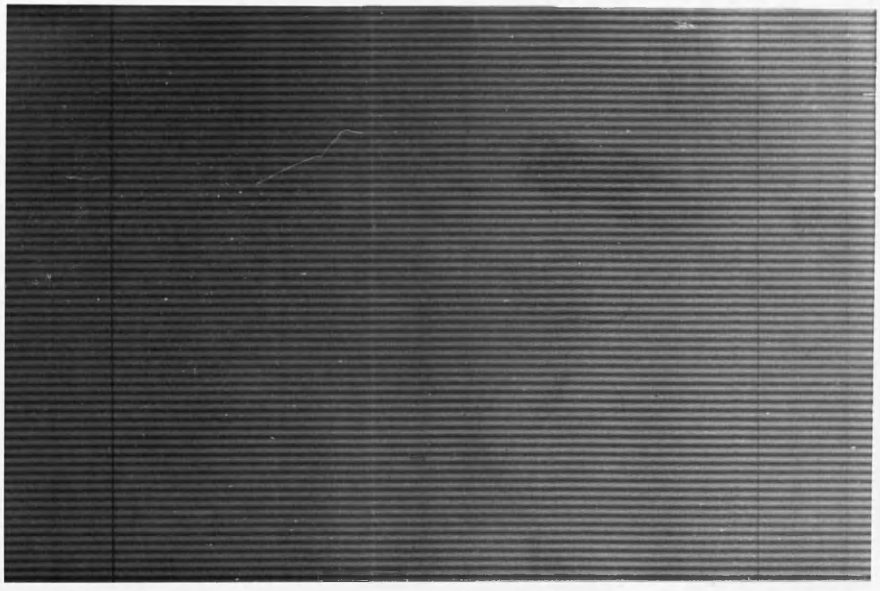


Figure 5.7

(a) Upper photograph. Interference pattern before addition of ethylene glycol.

(b) Lower photograph. Interference pattern after addition of ethylene glycol.





ployed, the two more dilute solutions being of similar, but different, concentration.

Prior to forming the diffusion boundaries, photographs were taken of the interference pattern from each limb. These patterns consisted of parallel fringes since there was no gradient of refractive index. The photographs were necessary to determine any correction to be applied to all subsequent photographs due to any slight imperfections in the optical system and cell.

After approximately two hours for thermal equilibration, the boundaries were formed in each limb and the centre section isolated. Photographs were taken at approximately 12 hour intervals over a period of 10-14 days, the typical duration of a diffusion experiment. Time was measured using two electric timers started soon after the boundaries had been formed.

At the end of an experiment, solutions were removed from each limb by syringe, thoroughly mixed, and analysed titrimetrically.[176]

5.3.4 Measurement of Fringes. Typical fringe patterns during the course of an experiment are shown in Figures 5.8a and b. The two vertical lines across these patterns result from the reference marks on the cell.

Photographic negatives of fringe patterns were measured using a Nikon model 6c overhead projector, which incorporated a travelling stage with manual drive and vernier scales for measuring the position of the stage to 0.01 mm. in both the longitudinal and transverse directions.

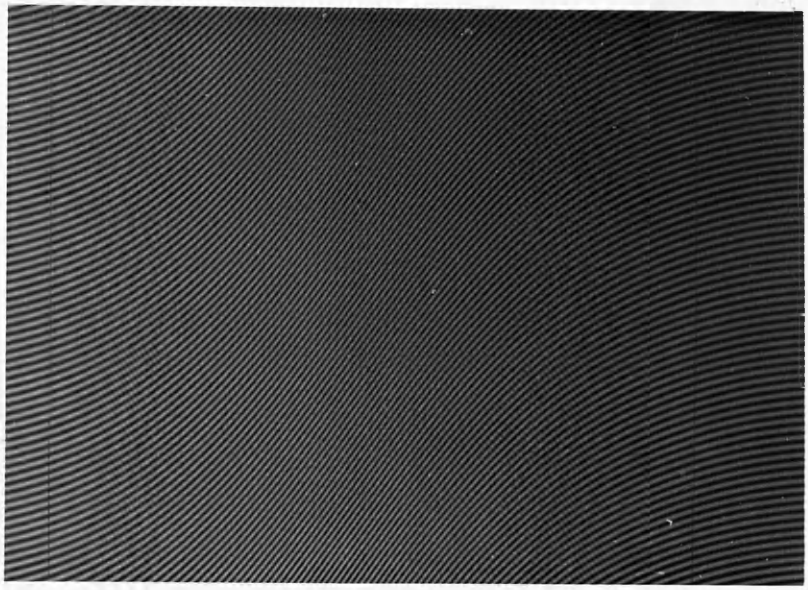
The photographic negative was placed between two thick, optical-quality glass plates and positioned on the stage so that the reference marks on the photograph appeared as vertical lines in the magnified image projected on to the screen. The position of the photograph was adjusted until cross-wires inscribed on the screen centred upon one reference line, this line being parallel to the direction of longitudinal movement of the stage.

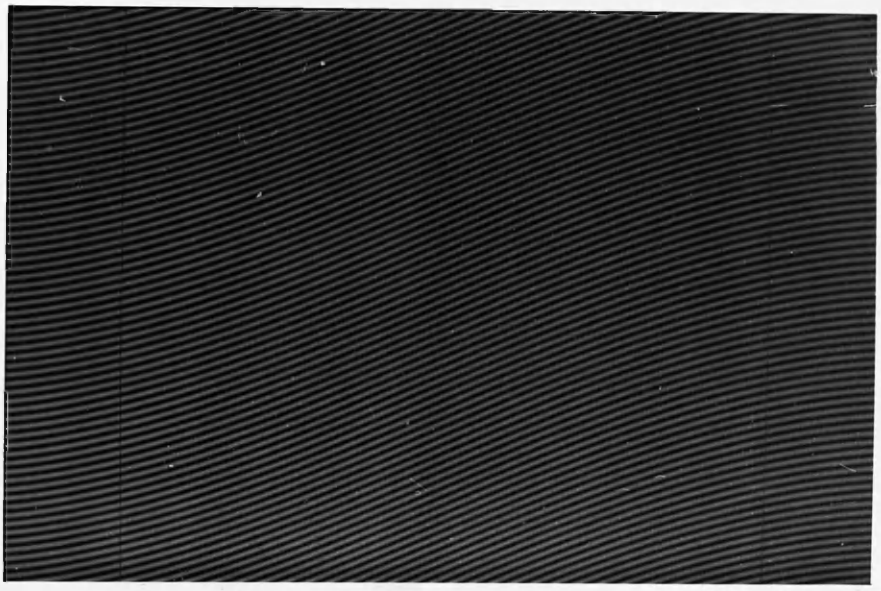
The mean width of a line was determined by setting the

Figure 5.8

(a) Upper photograph. Interference pattern soon after the commencement of a diffusion experiment.

(b) Lower photograph. Interference pattern towards the end of a diffusion experiment.





longitudinal vernier to zero and moving the stage longitudinally until 25 lines had been crossed, using the cross-wires on the screen as a point of reference. The vernier reading was noted and the mean width of a line calculated.

Setting the cross-wires on a point considered to be the centre of a fringe, again noting the longitudinal vernier reading, the stage was moved transversely until the cross-wires centred upon the other reference line. The integral number of fringes crossed on traversing the projection was noted. The partial fringe was determined by moving the stage longitudinally until the cross-wires centred upon the nearest fringe, and noting the vernier reading. The difference in vernier readings gave the partial shift in mm., which was then converted to a fraction of a fringe.

This method of fringe measurement was found to be reproducible to 0.05 mm., or 0.1 of a fringe.

Photographs of the uniform concentration profile in each limb before formation of the boundaries were measured in the same manner. Corrections due to slight deviations in parallelism of the fringes were applied to all subsequent photographs of each limb. Such corrections normally amounted to 0.1-0.3 of a fringe.

5.3.5 Treatment of Data. According to equation (5.3), the logarithm of the concentration difference between two reference lines will vary linearly with time, with a slope of $-D\pi^2/\ell^2$. Furthermore, any quantity which varies linearly with concentration will also follow this time dependence.

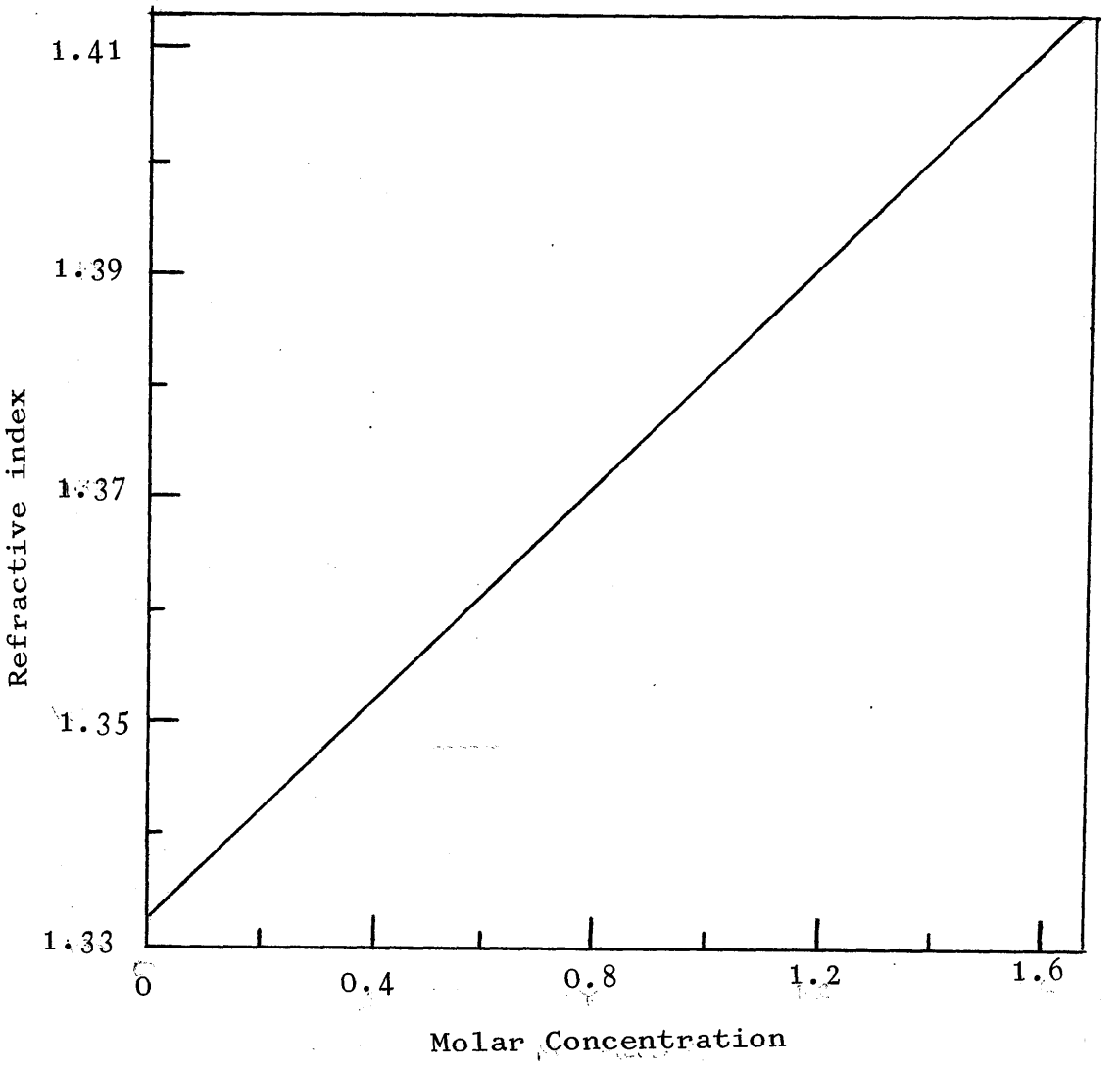
As shown in Figure 5.9, the refractive indices of cadmium iodide solutions are linear with respect to concentration over the range 0-1.6M,[64] and so the logarithm of the measured fringe shift will vary as $-D(\pi/\ell)^2$.

The measurement of fringe displacement, Δ, and time, t, were fitted to an equation of the form

$$\ln\Delta = x - yt$$

by the least squares method. The value of the diffusion coefficient was calculated from the relation $D = y(\ell/\pi)^2$.

Figure 5.9 Plot of refractive index versus concentration for cadmium iodide solutions.



5.4 Measurement of Transport Numbers by Concentration Cell Measurements.

5.4.1 Theoretical Considerations. The expression for the gradient of liquid junction or diffusion potential in terms of the transport numbers t_1^c and t_2^c, and the changes in the chemical potentials, $d\mu_1$ and $d\mu_2$, of the component ions 1 and 2, is given by equation (2.34):

$$F(-\partial\psi/\partial x) = (t_1^c/z_1).(\partial\mu_1/\partial x)+(t_2^c/z_2).(\partial\mu_2/\partial x)$$

where F is the Faraday and z_i the signed valency.

For a concentration cell of the form

$$Cd/Hg \;\Big|\; \underset{m=m'}{CdI_2} \;\Big\vdots\; \underset{m=m''}{CdI_2} \;\Big|\; Cd/Hg$$

the e.m.f. is given by the difference in internal potentials of the two electrdes.

$$E_{cell} = (\psi'_{Cd} - \psi''_{Cd}) = (\psi'_{Cd} - \psi'_s) + (\psi'_s - \psi''_s) - (\psi''_{Cd} - \psi''_s) \qquad (5.5)$$

where $(\psi'_s - \psi''_s)$ is the liquid junction potential and is the electrical potential difference between the two bulk solutions.

Integration of equation (2.34) between the limits ' and '' gives the expression for the liquid junction potential:

$$(\psi'_s - \psi''_s) = E_{LJ} = (T_1/z_1F)(\mu''_1 - \mu'_1) + (T_2/z_2F)(\mu''_2 - \mu'_2)$$

which reduces to

$$E_{LJ} = (RTT_1/z_1F).(\ln a'_1/a'_1) + (RTT_2/z_2F).(\ln a'_2/a'_2) \qquad (5.6)$$

T_1 and T_2 are defined as the integral transport numbers of cation and anion respectively.

For cadmium iodide, $z_1 = +2$ and $z_2 = -1$, and equation (5.6) becomes

$$E_{LJ} = (RTT_1/2F).(\ln a'_1/a'_1) - (RTT_2/F).(\ln a'_2/a'_2) \qquad (5.7)$$

For the half-cell Cd/Hg / $CdI_2(m')$, the e.m.f. is given by the Nernst equation,

$$E_{Cd} = E^{o}_{Cd} + (RT/2F).\ln a_1' \qquad (5.8)$$

Substitution of equations (5.7) and (5.8) in equation (5.5), and using the fact that $T_1 + T_2 = 1$, gives

$$E_{cell} = (RTT_2/2F).\ln a_1'.(a_2')^2/a_1''.(a_2'')^2 \qquad (5.9)$$

Substituting a = mf, where m is molality and f is the mean molal activity coefficient, equation (5.9) becomes

$$E_{cell} = (3kT_2/2).\ln (mf)'/(mf)''$$

where k = RT/F.

E.m.f. values for concentration cells of the form

$$Cd/Hg \;/\; CdI_2(m_1) \;\vdots\; CdI_2(m_2) \;/\; Cd/Hg$$

were measured. Cell transference numbers, t_2^c, were calculated from e.m.f. and activity coefficient data[9,39,156] by means of the relation[110]

$$t_2^c = (2F/3RT).dE_{cell}/d\ln(k/mf) \qquad (5.10)$$

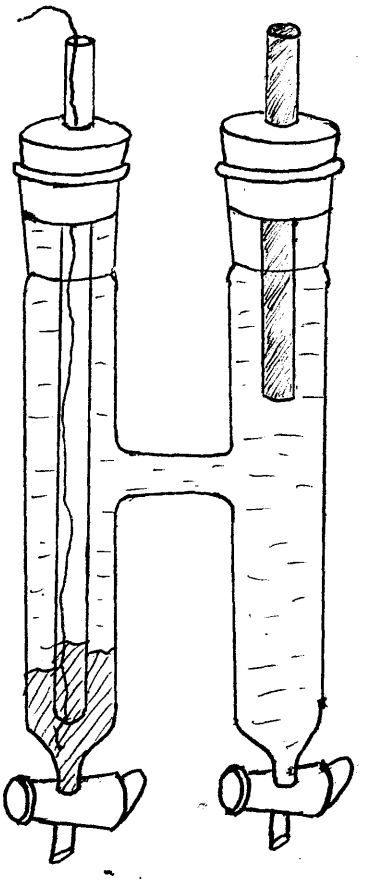
in which $k = (mf)_{m=0.001}$.

5.4.2 Preparation of Electrodes. Pure Cd/Hg amalgam was obtained by electrolysing the cadmium into the mercury, according to the method of Reilly and Ray.[147]

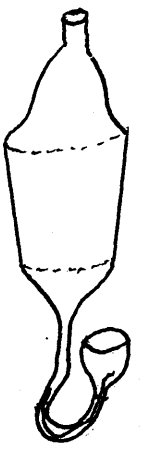
Into one limb of the vessel, (Figure 5.10a), was measured an accurately-weighed amount of doubly-distilled mercury. The electrolysing current was allowed to flow for approximately 95 hours, giving a 10% W/W amalgam. This was warmed to 60°C, thoroughly stirred, and transferred to an amalgam pipette. Thereafter it was melted down as needed and drawn into the electrode cups, (Figure 5.10b). Platinum wires sealed in the glass made contact with the external leads. Eight such elect-

Figure 5.10

(a) Preparation vessel for Cd/Hg amalgam.



(b) A Cd/Hg amalgam electrode.



rodes were made.

Bias potentials of these electrodes were measured in a 0.5M solution of cadmium iodide.. The average bias potential was found to be ±0.01mV. All bias potentials were monitored continuously throughout the series of experiments and were found to be independent of electrolyte concentration within the precision of measurement, ±0.01mV.

To test for any dependence of bias potential on amalgam composition, two electrodes of differing amalgam composition were made and the bias potentials of these were measured relative to one of the electrodes previously prepared. The results are shown in Table (5.1).

Silver-silver iodide electrodes were prepared according to the method of Ives and Janz,[65] and after preparation were allowed to stabilise for three days in the potassium iodide electrolysing solution. Bias potentials measured after this time were of the order of ± 0.4mV., becoming very much larger, 0.5-3.0mV., on transference to a solution of cadmium iodide.

Similar behaviour for this system has been observed by Bates,[9] and no explanation for the anomaly has yet been found. For this reason, silver iodide electrodes were not used in conjunction with cadmium iodide in the concentration cell.

5.4.3 The Concentration Cell. The cell design, shown in Figure 5.11, is that of Pikal and Miller.[140]

All experimental solutions were degassed for 30 minutes before use by bubbling purified nitrogen through the solutions. The nitrogen was presaturated by passing through distilled water and Dreschel bottles containing the experimental solutions.

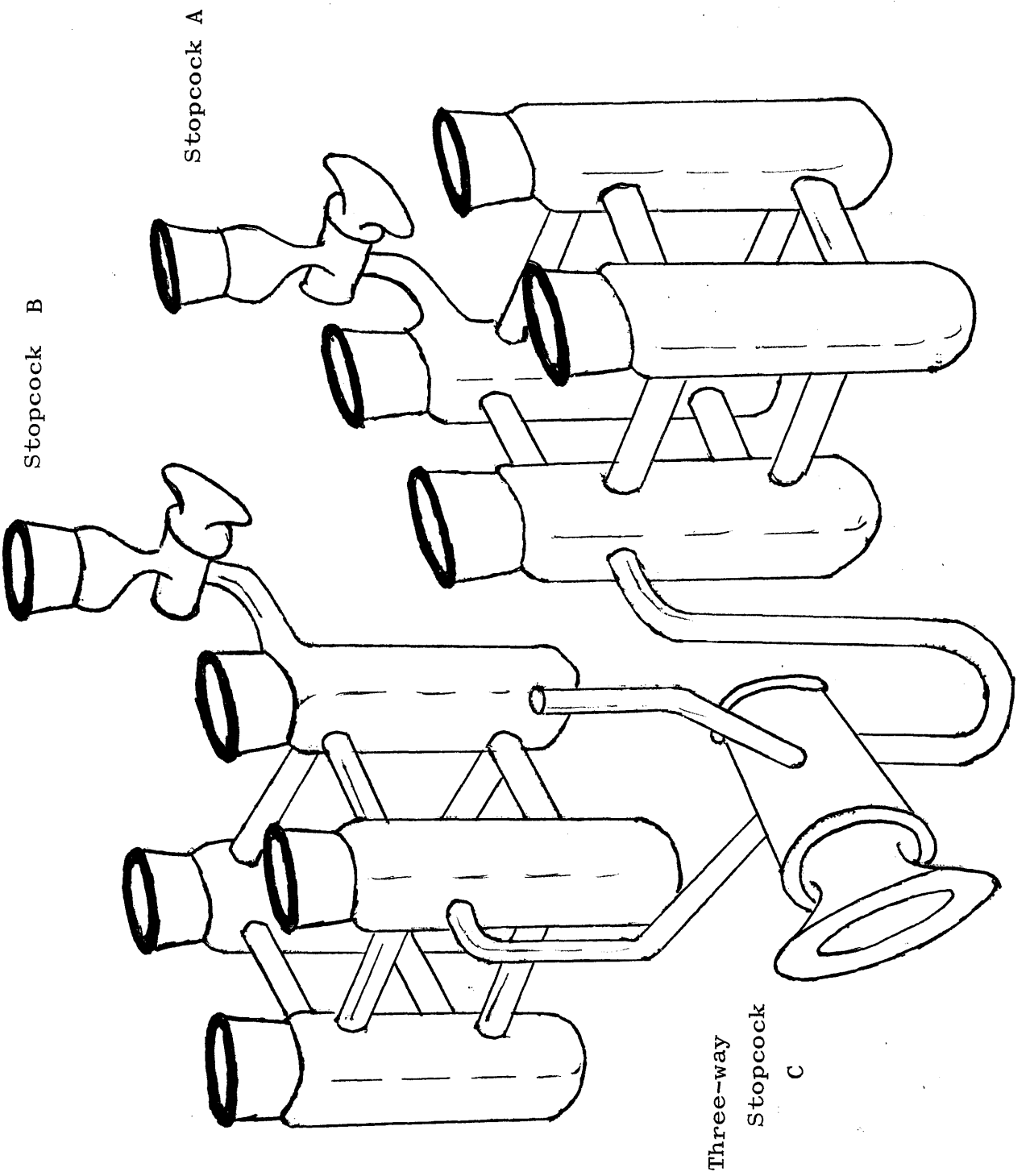
Amalgam electrodes were rinsed with dilute nitric acid to remove any oxide film, rinsed with distilled water, and pre-equilibrated for approximately 30 minutes in test-tubes containing the experimental solutions.

The cell, with electrodes in position, was flushed with nitrogen and filled with the experimental solutions of higher and lower concentrations through stopcocks A and B respectively. The liquid-liquid junction was formed by opening

Table (5.1) Dependence of bias potential on amalgam composition.

Electrode	Weight % Cd to wt. Hg in amalgam	Weight % Cd to total wt. amalgam	Bias potential (mV)
1	4.76	4.55	-3.16
2	7.00	6.54	0.01
3	10.00	9.09	0.01

Figure 5.11 The concentration cell.



large 120° three-way stopcock C. The filled cell was placed in a water thermostat maintained at 25°C ±0.01 and allowed to equilibrate for approximately one hour. The e.m.f. of the cell was measured at 15 minute intervals for a further period of two to three hours and was found to be invariant in that time within the precision of measurement. Stopcock C was closed after each measurement to minimise the possibility of diffusional mixing.

To minimise errors in e.m.f. due to heat of mixing at the liquid-liquid junction, the concentration difference between the two half-cells was kept less than 0.5 molal.

Bias potentials were measured regularly and were found to be <0.02 mV. E.m.f. measurements were made using a Solartron Digital Voltmeter LM 1867 with precision ±0.01 mV.

5.5 Measurement of Conductivity. Conductivity cells were of the Jones and Bollinger type,[71] the design being such that errors due to polarisation and shunt effects were eliminated.

Polarisation errors are avoided by the use of alternating currents and platinised electrodes.

Shunt effects[69,184] are eliminated by avoiding close proximity of the filling tubes and parts of the cell of opposite polarity.

Two Pyrex glass cells of cell constant 35.801 and 87.265 were used to investigate the concentration range 0.001-1.0M. Approximate cell dimensions are given in Table (5.2).

A schematic diagram of the cell is given in Figure 5.12. The bulbs incorporated in the filling tubes facilitated rinsing and filling the cells.

5.5.1 Platinisation of Electrodes. The platinising solution was that recommended by Jones and Bradshaw,[72] consisting of 0.025N HCl containing 0.3% platinic chloride and 0.025% lead acetate to improve the adherence of the deposit.[73]

5.5.2 Calibration of Cells. Calibration was carried out using 0.01, 0.1, and 1.0 Demal solutions of potassium chloride as recommended by Jones and Bradshaw.[72]

Quantities of potassium chloride required for 1 Kg. of

Table (5.2) Approximate dimensions of conductivity cells.

	Cell 1	Cell 2
h	10 cm.	15 cm.
D	1.6 cm.	1.6 cm.
l	7 cm.	12 cm.
n	14 cm.	14 cm.
V	15 ml.	20 ml.
β	35.801 ± 0.007	87.265 ± 0.010

h = distance between electrodes.

D = diameter of electrodes.

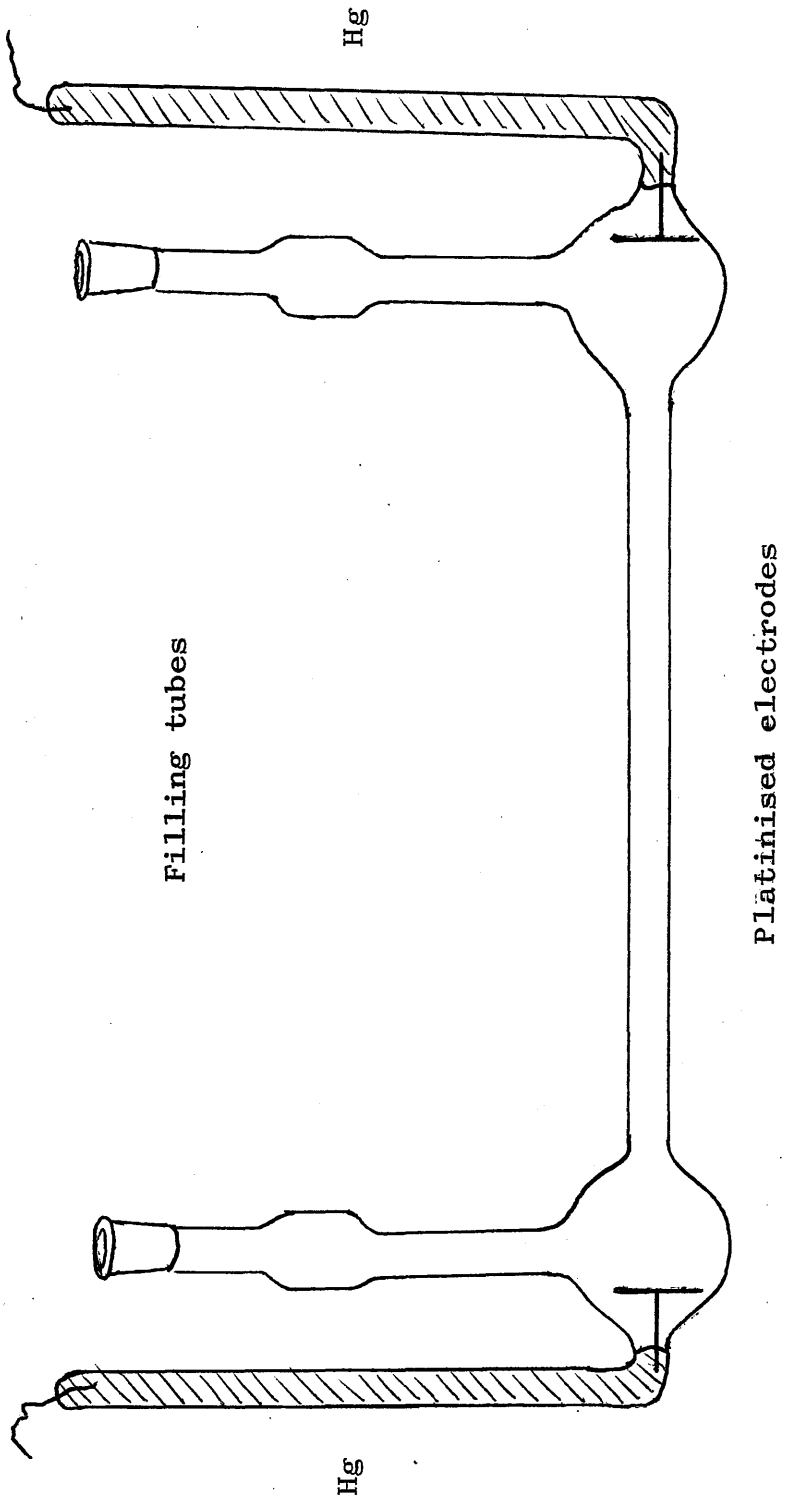
l = length of narrow portion between electrodes.

n = height of filling tubes.

V = approximate volume.

β = cell constant.

Figure 5.12 The Conductivity Cell.



solution, with the corresponding specific conductances, are given in Table (5.3). Normal vacuum corrections were applied to all weights. The solutions prepared were considered accurate to ±0.01%.

Cell 1 was calibrated using 0.01D and 0.1D solutions of KCl and was used only for solutions less concentrated than 0.1M. Cell 2 was calibrated using 0.1D and 1.0D KCl solutions and was used for solutions more concentrated than 0.1M.

The conductivity cells were re-calibrated every few months. The change in cell constant during this time was less than 0.1%.

5.5.3 Degassing of Solutions. All solutions more dilute than 0.1M were degassed for 30 minutes using purified nitrogen.

Comparison of the conductivities of degassed and undegassed samples of the same solution showed no difference when the samples were more concentrated than 0.05M. Degassing became increasingly important as the solutions became more dilute.

5.5.4 Constant Temperature Bath. The thermostat bath consisted of a tank filled with a light-weight non-conducting transformer oil heated by means of a light bulb and cooled by the controlled circulation of water through coiled copper tubing immersed in the bath.

Temperature was maintained at 25°C ±0.002 by means of a coiled glass mercury-toluene regulator and monitored using an E-mil TOT IMM standard thermometer, model K14047, calibrated to National Physical Laboratory standards.

5.5.5 The Conductance Bridge. Measurements were made using a digital autobalance precision bridge B331 manufactured by Wayne-Kerr Co. Ltd., incorporating a circuit which eliminated errors in resistance caused by the use of long connecting leads.

The bridge operated at a frequency of 1591.55 Hz., with provision for operation with an external frequency source.

Table (5.3) Weights of KCl required for, and specific conductances of, 1.0, 0.10, and 0.01 Demal solutions.

Solution (demal)	gm. KCl/Kgm. soln. (in vacuo)	specific conductance $(ohm.cm.)^{-1}$
1.00D	71.1352	0.11134_2
0.10D	7.41913	0.012856_0
0.01D	0.745263	0.0014087

An accuracy of $\pm 0.01\%$ was obtainable by operating six push-button decades, three for capacitance and three for conductance, which gave simultaneous digital displays.

5.5.6 Filling of Cells. Before filling, the cell was rinsed several times with 5 ml. aliquots of solution. The cell was then filled to a reference mark on the filling tubes, ensuring no air bubbles remained in the cell.

The cell was placed in the oil bath and, after thermal equilibrium had been established, readings were taken every few minutes until they were invariant.

Specific conductances, k, were calculated from the relation:

$$k = \beta/R$$

where β is the cell constant and $1/R$ is the conductance. After correction for the conductance of the water, the equivalent conductance, Λ, was calculated from

$$\Lambda = 1000k/N$$

where N is the concentration in equivalents/litre.

5.5.7 Measurements with External Frequency Source. According to Jones and Bollinger,[71] the frequency dependence of conductance is given by the relationship

$$R_p = R_t - R_t^2 . R_p . \omega^2 . C_p^2 \qquad (5.11)$$

where R_p is the apparent resistance, R_t the true resistance, ω the angular frequency in Hz., and C_p the capacitance in farads.

If $R_p \cong R_t$, equation (5.11) becomes

$$R_p = R_t - R_p^3 . \omega^2 . C_p^2 \qquad (5.12)$$

Since R_p varies from 30-5000 ohms, and C_p is of the order of 10^{-12} farads, then, for the frequency range 1000 to 4000

Hertz, the error $R = R_p^3 . {}^2 . C_p^2$ is negligibly small, much less than 0.01%. Theoretically, an error of this magnitude cannot be observed on the instrument.

It was found impossible to verify this, however, since readings using an external source oscillated by $\pm 0.5\%$. The cause of this was probably local electrical interference from other instruments in the laboratory, and it was necessary to assume no frequency dependence.

CHAPTER 6

RESULTS OF TRANSPORT EXPERIMENTS AND DISCUSSION OF THE IRREVERSIBLE THERMODYNAMIC ANALYSIS OF THE SYSTEM CdI_2-H_2O

6.1 Results of Diffusion Measurements.

The results of diffusion measurements using cadmium iodide solutions are given in Table (6.1) and shown graphically in Figure 6.1. Also shown in Figure 6.1 are the results of earlier diffusion measurements by Garland, Tong, and Stockmayer [37] using the porous frit method, and by McBain, van Rysselberghe, and Squance [101] using the diaphragm cell technique. Porous frit data may be considered accurate to approximately ± 5%, though the accuracy of the latter data must be considered doubtful, since no method of stirring the solutions in the diffusion cell was employed. Diffusion data obtained in this work were considered accurate to ± 0.3%.

6.2 Results of Concentration Cell Measurements.

Experimental emf values in millivolts for concentration cells of the form

$$\mathrm{Cd/Hg} \;\big|\; \mathrm{CdI_2}\ (m_1) \;\big\vert\; \mathrm{CdI_2}(m_2) \;\big|\; \mathrm{Cd/Hg}$$

are given in Table (6.2). Every value represents the mean of at least 16 individual voltage measurements. The last column gives the standard deviation from the mean, σ , in millivolts, corresponding to each mean emf. For the calculation of emf transference numbers, emf values for concentration cells of the form

$$\mathrm{Cd/Hg} \;\big|\; \mathrm{CdI_2}(m=0.001) \;\big\vert\; \mathrm{CdI_2}(m) \;\big|\; \mathrm{Cd/Hg}$$

are required. Combination of the emf's of experimentally measured concentration cells from Table (6.2) gave values for cells symbolised by that above; these values are given in Table (6.3). Whenever there was more than one way to combine the emf's, all possible combinations were averaged. The estimated error is ± 0.3%.

Transport numbers were obtained using equation (5.7), which necessitated calculation of the term

Table (6.1) Diffusion coefficients for CdI_2.

Concentration (M)	$10^5 D$ (1)	(2)	(3)
0.005	0.959	-	-
0.00501	-	-	1.181
0.00724	-	-	1.128
0.0096	-	0.873	-
0.01	0.859	-	-
0.03889	-	-	0.814
0.0414	-	0.855	-
0.04397	-	-	0.810
0.05	0.789	-	-
0.080	-	0.824	-
0.083	-	0.834	-
0.09339	-	-	0.787
0.09439	-	-	0.779
0.121	-	0.808	-
0.15	0.732	-	-
0.160	-	0.807	-
0.1729	-	-	0.754
0.1781	-	-	0.750
0.2419	-	-	0.738
0.2515	-	-	0.734
0.292	-	0.768	-
0.4572	-	-	0.719
0.500	0.690	0.785	-
0.6037	-	-	0.727
0.7896	-	-	0.754
0.7936	-	-	0.761
0.947	-	0.809	-
0.9713	-	-	0.798
0.9796	-	-	0.801

(1) Reference 101

(2) Reference 37

(3) This work

Figure 6.1 Diffusion Coefficients for CdI_2.

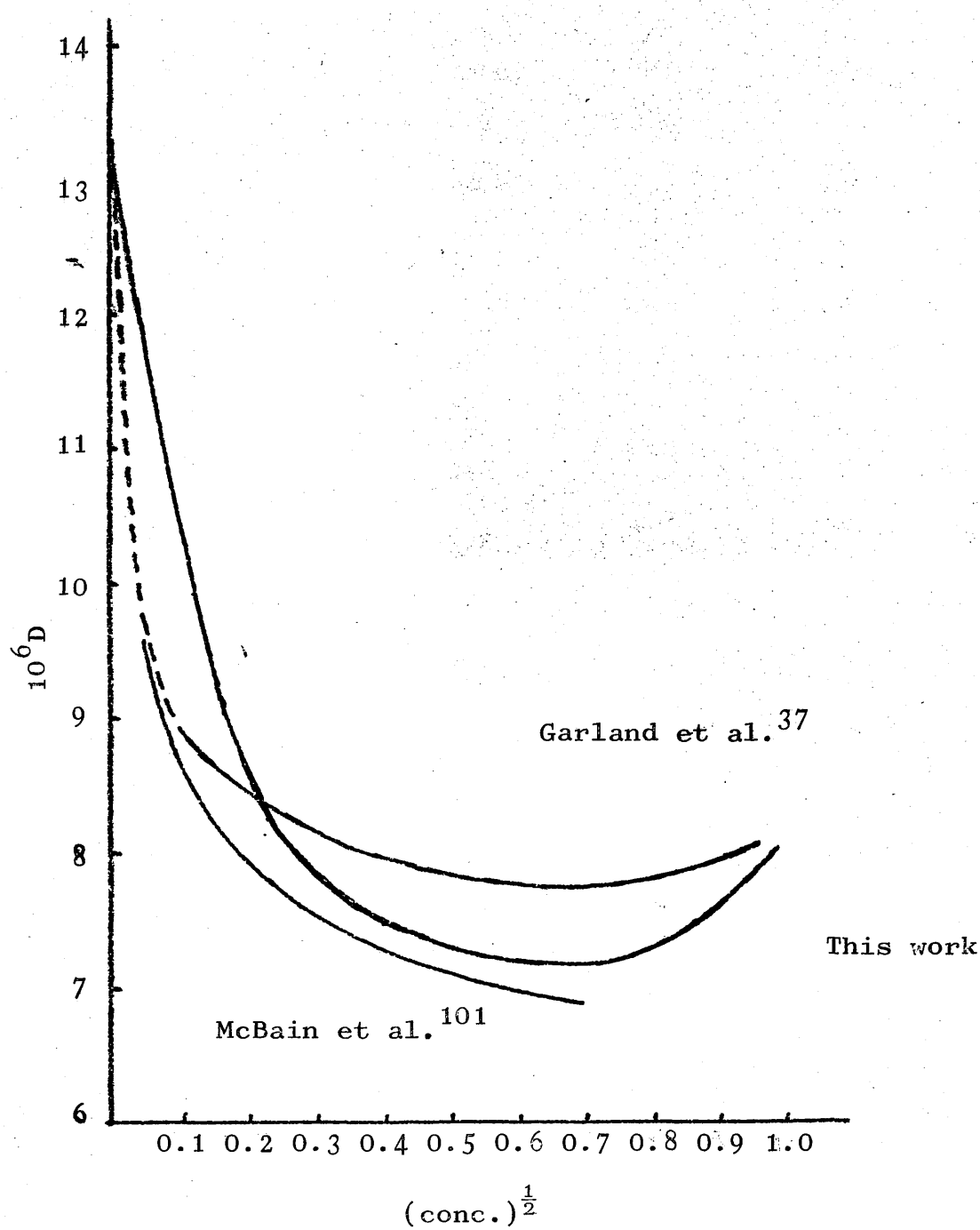


Table (6.2).

Potentials of CdI_2 concentration cells of the type

Cd/Hg / $CdI_2(m_1)$ ¦ $CdI_2(m_2)$ / Cd/Hg

m_1	m_2	E.m.f.(mV.)	σ(mV.)
0.0009747	0.004981	-26.18	0.07
0.0009747	0.0099599	-35.90	0.02
0.004981	0.0099599	- 9.83	0.01
0.004981	0.049572	-27.70	0.05
0.0099599	0.049572	-18.09	0.02
0.0099599	0.099138	-25.32	0.03
0.049572	0.099138	- 7.17	0.02
0.19822	0.41058	- 9.86	0.02
0.099138	0.19822	- 8.00	0.03
0.099138	0.41058	-17.85	0.02
0.29971	0.41058	- 4.58	0.01
0.19822	0.29971	- 5.38	0.01
0.099138	0.29971	-13.36	0.01
0.29971	0.65303	-11.82	0.02
0.41058	0.65303	- 7.28	0.01
0.41058	0.90705	-17.39	0.02
0.65303	0.90705	-10.11	0.03
0.65303	1.10493	-13.43	0.03
0.90705	1.10493	- 3.32	0.04

Table (6.3).

Potentials of CdI_2 concentration cells of the type

$$Cd/Hg \;/\; CdI_2(m=0.001) \;\vdots\; CdI_2(m) \;/\; Cd/Hg$$

m	E.m.f.(mV.)
0.004981	-26.18
0.0099599	-35.96
0.049572	-54.05
0.099138	-61.25
0.19822	-69.25
0.29971	-74.62
0.41058	-79.16
0.65303	-86.44
0.90705	-96.55
1.10493	-99.87

$$(3RT/2F)\ \ln(k/mf)$$

where $k=(mf)_{m=0.001}$. Since Ag-AgI electrodes could not be used, activity data were obtained from the literature [7,39,156] and curve-fitted by the method of least squares. Coefficients of this curve-fit between lnf and m, and between lnf and lnm, are given in Appendix 1. The activity data were used to calculate $(3RT/2F)\ln(k/mf)$, and the resulting values were curve-fitted against their corresponding emf values, again by the method of least squares. The resulting polynomial was of the form

$$E_{cell} = 0.411353x-5.549613x^2-78.60436x^3 -390.65362x^4 \qquad (6.1)$$

where $x = (3RT/2F)\ln(k/mf)$.
Equation (6.1) reproduced experimental values of E_{cell} to an accuracy of $\pm$ 0.1%. Differentiation of equation (6.1) gives:

$$d(E_{cell})/dx = 0.411353-11.099x-235.81x^2 -1562.5x^3 \qquad (6.2)$$

and since $x = (3RT/2F)\ln(k/mf)$, then

$$dE/dx = (2F/3RT).dE/d\ln(k/mf) \ = t_2^c = 1-t_1^c$$

from equation (5.7). Transport numbers obtained in this way were interpolated to round-number concentrations, and are given in Table (6.4). For comparison, the results of Sahay,[159] using the moving boundary method, are also shown; the values differ by up to 5%. In order to ascertain whether this discrepancy reflected a true experimental difference, or whether the difference was due merely to the method of differentiating equation (6.1), values of t_1^c were evaluated using the method of Rutledge.[157] Rutledge's method

Table (6.4).

Transport numbers for CdI_2.

m	t_1^c	t_1^{c*}	t_1^{c**}
0.005	0.431	0.450	0.435
0.010	0.416	0.448	0.420
0.050	0.311	0.321	0.314
0.100	0.205	--	0.201
0.200	0.053	--	0.057
0.300	-0.051	--	-0.049
0.400	-0.135	--	-0.139
0.500	-0.213	--	-0.218
0.600	-0.290	--	-0.291
0.700	-0.365	--	-0.362
0.800	-0.436	--	-0.433
0.900	-0.499	--	-0.499
1.000	-0.556	--	-0.559

* J.N.Sahay, J.Sci.In.Res., 18B, 235, (1959).

** Calculated by the method of Rutledge.
(G.Rutledge, Phys.Rev., 40, 262, (1932)).

evaluates the differential of the function y=f(n), values of dy/dn being found from values of y observed at equally-spaced intervals of n. The differentiating tool used is a fourth degree polynomial; it is applied successively to sets of five consecutive data points. It is not implied that the data as a whole may be adequately represented by a polynomial or any other elementary type of function.

If the five values of n, (n_{-2}, n_{-1}, n_0, n_1, and n_2) are spaced at equal intervals, h, so that

$$h = n_2-n_1 = n_1-n_0 = n_0-n_{-1} = \ldots\ldots \text{ etc.}$$

and the five corresponding values of y are y_{-2}, y_{-1}, y_0, y_1, and y_2, then the derivative at the points -1, 0, and 1 is given by:

$$(dy/dn)_{n=n_{-1}} = (1/12h)(-3y_{-2}-10y_{-1}+18y_0-6y_1+y_2)$$

$$(dy/dn)_{n=n_0} = (1/12h)(y_{-2}-8y_{-1}+8y_1-y_2)$$

$$(dy/dn)_{n=n_1} = (1/12h)(-y_{-2}+6y_{-1}-18y_0+10y_1+3y_2)$$

A computer programme, given in Appendix 2, was used to evaluate t_1^c by the above method over the concentration range 0.001-1.0M. The results, shown in Table (6.4), indicate a true experimental difference between this work and the results of Sahay.[159]

6.3 Results of Conductivity Measurements.

Tables (6.5) and (6.6) summarise the results of conductance measurements in dilute (<0.1M) and concentrated solutions respectively.

Interpolated values of Λ from this work are compared, in Table (6.7), with the literature values of Rabinowitsch [146] and van Rysselberghe, Grunnell, and Carlson.[158] Agreement with Rabinowitsch's data is excellent, within $\pm$ 0.2% in all cases, though poorer agreement is obtained with the more recent data of

Table (6.5).

Conductivities of CdI_2 solutions; 0.001-0.1M.

Molar Concentration	Equivalent Conductivity
0.001114	103.2_0
0.002109	92.19
0.002998	87.37
0.004654	76.24
0.006109	71.42
0.008271	66.15
0.010919	61.03
0.019475	50.94
0.042019	38.53
0.058696	33.93
0.079468	30.36
0.091171	28.94
0.102582	27.73

Table (6.6).

Conductivities of CdI_2 solutions, 0.1-1.0M.

Molar Concentration	Equivalent Conductivity
0.13908	25.21
0.15347	24.60
0.16767	23.72
0.19905	22.83
0.23773	21.48
0.27912	20.81
0.32407	19.84
0.32819	19.83
0.35372	19.44
0.36259	19.32
0.36728	19.30
0.38331	19.10
0.40583	18.78
0.49850	17.82
0.50186	17.80
0.55483	17.33
0.58499	16.86
0.59384	16.85
0.64556	16.41
0.65589	16.36
0.66870	16.30
0.76342	15.69
0.78576	15.46
0.84731	15.12
0.93592	14.58

Table (6.7) Experimental and literature conductance data for CdI_2.

Concentration (M)	*	**	(1)
0.1385	25.33	-	25.30
0.25	-	21.4	21.28
0.282	20.65	-	20.63
0.435	18.46	-	18.45
0.50	-	17.81	17.81
0.615	16.73	-	16.71
0.855	15.07	-	15.08
1.00	-	14.18	14.30

* reference 146

** reference 158

(1) this work (interpolated)

van Rysselberghe.

6.4 Irreversible Thermodynamic Analysis of Results.

The results of diffusion, concentration cell, and conductivity measurements complete the parameters required for an irreversible thermodynamic analysis for the system CdI_2-H_2O over the concentration range 0.001-1.0M.

For calculation of the L_{ij} and R_{ij}, the activity correction term, $(1+m d\ln f/dm)$, was evaluated over the full concentration range by differentiation of an nth. degree empirical fit between lnf and lnm:

$$\ln f = a_0 + \sum_{i=1}^{n} a_i (\ln m)^i \qquad (6.3)$$

Two such equations were used, covering the concentration ranges 0.001-0.1M and 0.1-1.0M. The coefficients a_i for both equations are given in Table (6.8). Values of the function $(1+m d\ln f/dm)$ given in Table (6.9) were obtained by differentiation of equation (6.3) by the method of Rutledge described previously.

A computer programme was used to calculate the phenomenological coefficients, L_{ij} and R_{ij}, from the transport data. This programme, given in Appendix 2, reproduced Miller's [108] data for several systems to $\pm$ 0.1%.

The mobility coefficients, $L_{ij}(i,j=1,2)$, were calculated from equation (2.45), and the frictional coefficients, $R_{ij}(i,j=1,2)$, were obtained by matrix inversion of the L_{ij}. The ion-solvent frictional coefficients, $R_{i0}(i=1,2)$, were calculated from the R_{ij} using the relations defined by equation (2.19).

The results are presented in Table (6.9), in which S is the formal ionic strength of the solution. In this Table, infinite dilution values for the quantities D and Λ were calculated by combining the literature value for $\lambda^0_{I^-}$ with the value for $\lambda^0_{Cd^{2+}}$ obtained from the (extrapolated) transport number of cadmium ion at infinite dilution by means of the

Table (6.8) Coefficients of equation (6.3).

Coefficients	0.001-0.1M	0.1-1.0M
a_0	-3.322705	-3.684670
a_1	-0.103363	-0.538461
a_2	0.258200	0.081779
a_3	0.047974	0.018005
a_4	0.002432	-

Table (6.9) (overleaf)

Phenomenological coefficients for CdI_2.

'Act. term' in these tables refers to the quantity (1+mdlnf/dm).

Data at infinite dilution is extrapolated.

SqrtS* x 10	c	m	Eq.Cond.	t_+	$10^5.D$	Act. term	10^{12} x L_{11}/N	10^{12} x L_{12}/N	10^{12} x L_{22}/N
0.0000	0.0000	0.000000	135.71	0.434	1.331	1.000	1.5826	0.0000	8.2545
1.2247	0.0050	0.005015	74.86	0.431	1.187	0.753	1.4329	1.1332	6.8412
1.7321	0.0100	0.010033	62.63	0.416	1.076	0.629	1.4576	1.5161	6.9606
3.8730	0.0500	0.050296	36.06	0.310	0.806	0.379	1.5218	2.4433	7.5590
5.4772	0.1000	0.100926	28.36	0.203	0.780	0.352	1.5214	2.7336	7.8948
7.7460	0.2000	0.203215	22.64	0.049	0.746	0.338	1,4851	2.9106	8.1336
9.4868	0.3000	0.306912	20.32	-0.057	0.728	0.344	1.4258	2.9139	8.1345
10.9545	0.4000	0.412065	18.87	-0.145	0.720	0.359	1.3591	2.8651	8.0507
12.2474	0.5000	0.518723	17.81	-0.227	0.720	0.378	1.3071	2.8313	8.0096
13.4164	0.6000	0.626929	16.87	-0.311	0.727	0.397	1.2751	2.8320	8.0394
14.4914	0.7000	0.736734	16.07	-0.392	0.740	0.417	1.2605	2.8593	8.1211
15.4919	0.8000	0.848183	15.41	-0.467	0.760	0.436	1.2620	2.9105	8.2489
16.4317	0.9000	0.961324	14.80	-0.534	0.783	0.455	1.2699	2.9642	8.3668
17.3205	1.0000	1.076203	14.30	-0.600	0.804	0.474	1.2791	3.0189	8.4950

SqrtS* x 10	10^{-11} x NR_{11}	$-NR_{12}$ $\times 10^{-11}$	NR_{22} $\times 10^{-11}$	$-R_{10}$ $\times 10^{-9}$	$-R_{20}$ $\times 10^{-9}$	$+C_oR_{10}$ $\times 10^{-11}$	$-C_oR_{20}$ $\times 10^{-11}$	R_{00}/N $\times 10^{-7}$
0.0000	6.3186	0.0000	1.2115	5.7088	2,1891	3.1593	1.2115	9.1136
1.2247	8.0308	1.3302	1.6821	4.8543	1.8385	2.6852	1.0170	7.7117
1.7321	8.8701	1.9321	1.8575	4.5226	1.6108	2.5030	0.8915	6.9966
3.8730	13.6600	4.4156	2.7502	4.3729	0.9823	2.4147	0.5424	5.7386
5.4772	17.3960	6.0233	3.3523	4.8606	0.6190	2.6745	0.3406	5.5418
7.7460	22.5460	8.0682	4.1166	5.8662	0.1511	3.2050	0.0826	5.6452
9.4868	26.1740	9.3758	4.5878	6.8407	-0.1846	3.7112	-0.1002	5.9646
10.9545	29.4600	10.4840	4.9732	7.8809	-0.4990	4.2457	-0.2688	6.3880
12.2474	32.6510	11.5420	5.3284	8.9425	-0.8272	4.7838	-0.4425	6.8119
13.4164	36.0350	12.6940	5.7156	10.0220	-1.1888	5.3235	-0.6314	7.1963
14.4914	39.4010	13.8730	6.1157	11.0520	-1.5561	5.8281	-0.8206	7.5274
15.4919	42.5350	15.0080	6.5074	11.9570	-1.9032	6.3598	-0.9964	7.7842
16.4317	45.5100	16.1240	6.9075	12.7610	-2,2211	6.6316	-1.1543	8.0036
17.3205	48.4840	17.2300	7.3000	13.5950	-2.5490	7.0124	-1.3148	8.2363

* S refers to the ionic strength.

relation

$$t_1^0 = \lambda_1^0/(\lambda_1^0 + \lambda_2^0) = \lambda_1^0/\Lambda_0$$

The value of λ_1^0 obtained in this way was 58.9 ohm^{-1} $cm^2.equiv.^{-1}$, with an estimated uncertainty of approximately $\pm$ 1%.

No reliable estimate of λ_1^0 for cadmium ion exists in the literature, though Garland, Tong, and Stockmayer [37] used the value for Mg^{2+} ($53.0 ohm^{-1} cm^2.equiv.^{-1}$), since the conductivities of CdI_2 and MgI_2 solutions are almost identical at 18°C. A value of 61.6 ohm^{-1} $cm^2.equiv.^{-1}$ was used by McBain, van Rysselberghe, and Squance [101] and a value of $53.8 ohm^{-1} cm^2.equiv.^{-1}$ is available [84], but must be considered unreliable since it is omitted from both Robinson and Stokes' [151] and Harned and Owen's [59] classic textbooks. However, the present diffusion work suggests that the estimate of $53.0 ohm^{-1} cm^2.equiv.^{-1}$ is too low and that the true value of λ_1^0 for Cd^{2+} lies in the range 58-60 ohm^{-1} $cm^2.equiv.^{-1}$, close to the values of λ_1^0 for Ca^{2+} and Sr^{2+} of 59.50 and 59.4_5 $ohm^{-1} cm^2.equiv.^{-1}$ respectively. Accordingly, D^0 was calculated using the Nernst expression, with λ_1^0 taken as 58.9 $ohm^{-1} cm^2.equiv.^{-1}$

Since the L_{ij} are intrinsically more fundamental than the measurable transport parameters of diffusion coefficient, transport number, and conductivity, a study of their behaviour with concentration gives a more detailed insight into the processes occurring in solution.

Although very few systems of 2:1 electrolytes have been investigated, there exist sufficient data for calcium chloride [108] and cadmium chloride ** for some general comparisons to be made.

Calcium chloride is a completely dissociated salt in solution; the intrinsic mobility of Ca^{2+} ion at infinite dilution being $1.597.10^{-12}$ $moles^2/joule.sec.cm.$, which compares closely with the value of $1.58.10^{-12}$

** A.J.McQuillan J.Chem.Soc.Far.Trans.1,8,1558,(1974)

moles^2/joule.sec.cm. estimated for Cd^{2+}. In addition, the mobilities of chloride and iodide ions are almost identical.[155] The major difference between the two electrolytes lies in the self-complexing behaviour of cadmium iodide solutions.

A more direct comparison may be made with cadmium chloride, since self-complexing also occurs in this system, though to a considerably lesser extent. A measure of the relative degree of complexing in the two systems may be inferred from the fact that t_1^c becomes zero at a concentration of approximately 0.25m in CdI_2 and approximately 2m in $CdCl_2$. Figures 6.2, 6.3, and 6.4 show the variation of the L_{ij} with concentration for the three systems.

The direct mobility coefficient, $L_{ii}(i=1,2)$, is a measure of the mobility which an ion would have in the absence of interactions with oppositely-charged ions. The L_{ii} includes a large obstruction contribution, as well as smaller effects such as the coulombic interaction of other i-type ions, solvation, and reference-frame interactions with the solvent.[108] In dilute solution, the intrinsic mobility of Cd^{2+} in CdI_2 decreases rapidly from its value at infinite dilution, in common with the trend observed for Ca^{2+} in $CaCl_2$, though with steeper slope. At higher concentrations, however, L_{11}/N for Cd^{2+} in CdI_2 increases to a maximum at approximately 0.25M, thereafter showing a general decrease with increasing concentration. This behaviour is anomalous in that the intrinsic mobilities of most salts show a steady decrease with increasing concentration,[66] as exemplified by L_{11}/N for Cd^{2+} in $CdCl_2$.

The intrinsic mobility of I^- in CdI_2 exhibits the same anomalous behaviour as cadmium ion in CdI_2, with an initial sharp decrease at low concentration and a substantial increase at higher concentrations. Both $CaCl_2$ and $CdCl_2$ show a similar decrease at low concentration which continues to higher concentrations.

Figure 6.2 Variation of L_{11}/N with concentration for $CaCl_2$, $CdCl_2$, and CdI_2.

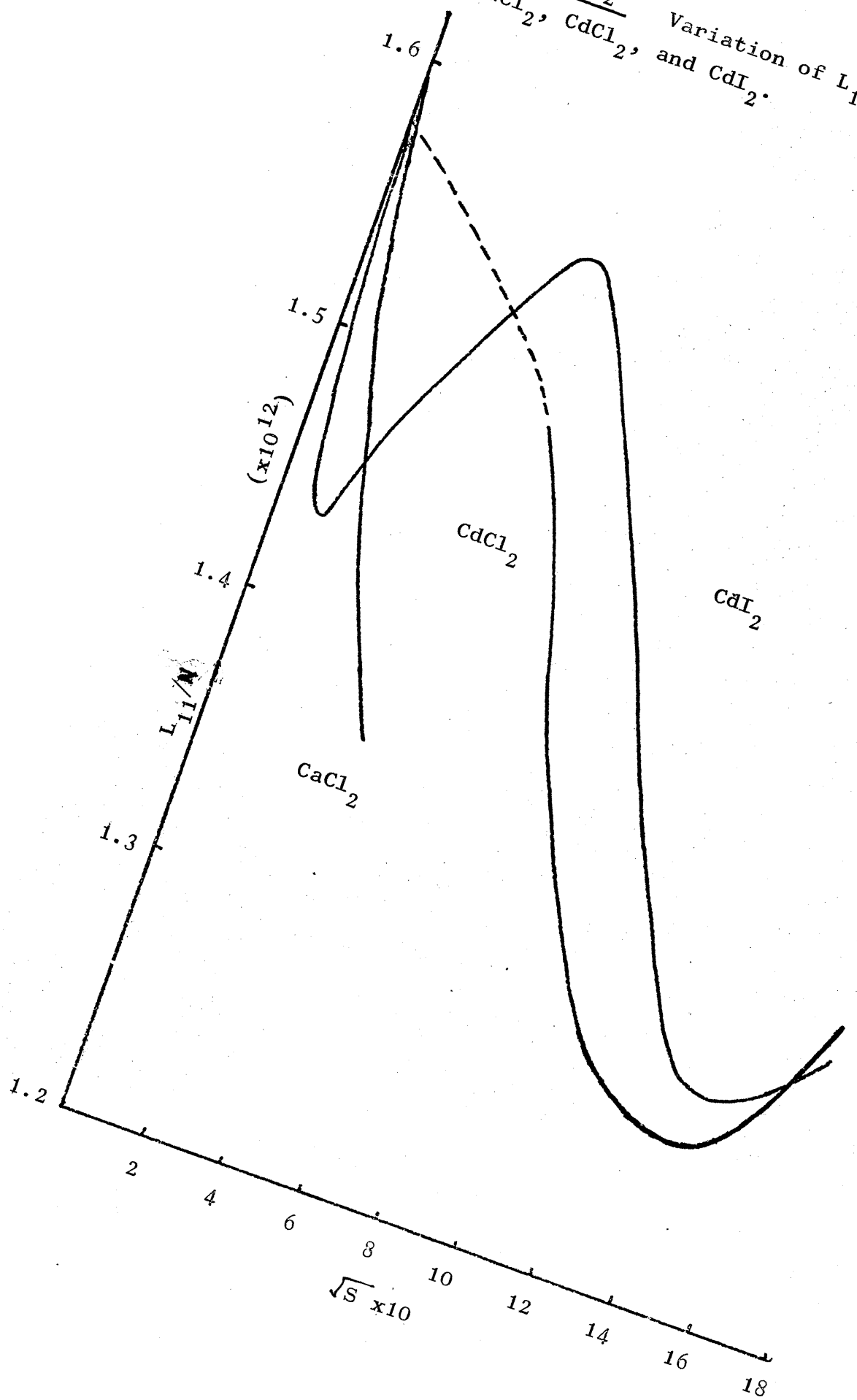


Figure 6.3 Variation of L_{22}/N with concentration for $CaCl_2$, $CdCl_2$, and CdI_2.

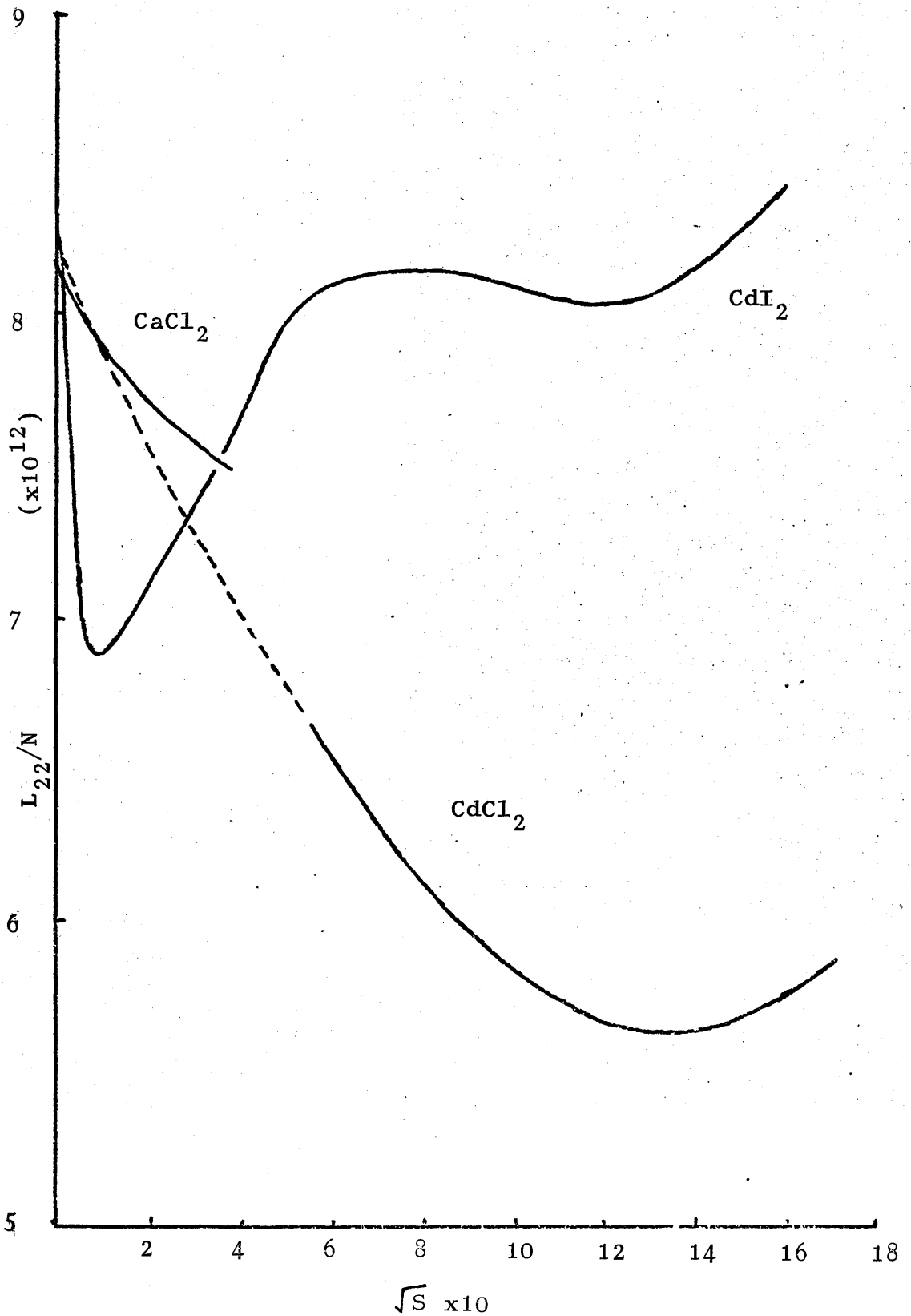
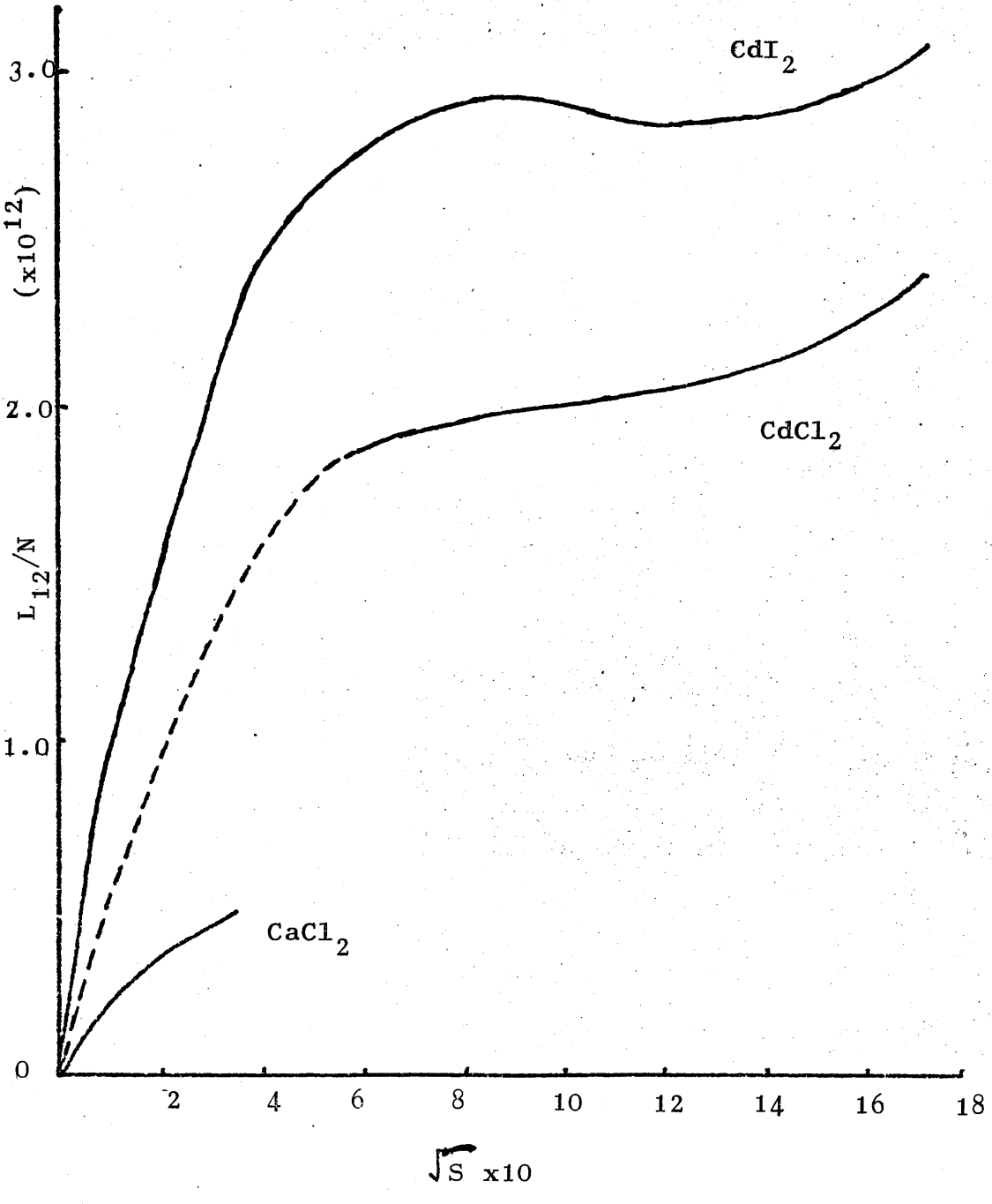


Figure 6.4 Variation of L_{12}/N with concentration for $CaCl_2$, $CdCl_2$, and CdI_2.



A rigourous analysis of a situation as complex as that which exists in aqueous cadmium iodide solutions cannot be made at this time. However, Pikal's[142] analysis of ion-pair formation in simple electrolyte systems of symmetrical salts indicates that complexing of this type will decrease the intrinsic mobilities of the component ions. Similarly, a larger degree of ion association in the form of neutral ion pair- or charged complex-formation may explain to a large extent the observed sequence of the coupling coefficients, L_{12}/N.

$$CdI_2 > CdCl_2 > CaCl_2$$

6.5 Self-Complexing in Cadmium Iodide Solutions.

Equilibria in solutions of cadmium iodide have been investigated by McBain, van Rysselberghe, and Squance,[101] Riley and Gallafent,[150] and Bates and Vosburgh.[8] In the latter work, the stability constants for the species CdI^+, CdI_2, CdI_3^-, and CdI_4^{2-} are reported. The stability constants are defined by equations (6.4)-(6.7),

$$\beta_1 = C_{CdI^+}/C_{Cd^{2+}}.C_{I^-} \qquad (6.4)$$

$$\beta_2 = C_{CdI_2}/C_{Cd^{2+}}.C_{I^-}^2 \qquad (6.5)$$

$$\beta_3 = C_{CdI_3^-}/C_{Cd^{2+}}.C_{I^-}^3 \qquad (6.6)$$

$$\beta_4 = C_{CdI_4^{2-}}/C_{Cd^{2+}}.C_{I^-}^4 \qquad (6.7)$$

and are related to the concentrations, C , of the various complex species in solution.

Using the values for $\beta_1, \beta_2, \beta_3$, and β_4 of Bates and Vosburgh, and the activity correction data of Reilly and Stokes [148] for $CdCl_2$, the concentrations of each species present at various bulk salt concentrations were calculated. The results are given in Table (6.10).

The activity correction data of Reilly and Stokes[148] was taken since these authors have cast some doubt on the original activity correction procedure of Bates and Vosburgh. In the latter work, the activity correction involved the use of activity coefficients calculated on the assumption that a simple Debye-Hückel type of equation was obeyed. The use of this type of equation is questionable, since it is applicable only at quite low ionic strengths and to ions of only one valency type. The data of Reilly and Stokes are not open to the same objections.[148] Data for $CdCl_2$ were chosen on a 'good guess' basis, since no equivalent data were available for CdI_2.

6.5.1 Irreversible Thermodynamic Representation.

A solution of cadmium iodide may be considered to contain six species: Cd^{2+}, CdI^+, CdI_2, CdI_3^-, CdI_4^{2-}, and free iodide ion. Denoting these species by the subscripts 0,1,2,3,4, and i, respectively, then the dissipation function, Φ, may be defined in terms of the solvent-fixed flows, j, and the forces, x, for each of the species in solution. Thus

$$\Phi = T\sigma = j_0x_0+j_1x_1+j_2x_2+j_3x_3+j_4x_4+j_ix_i \qquad (6.8)$$

Considering each complex species to be in local equilibrium with cadmium and iodide ions, then the phenomenological equations are given by equation (2.16).

$$j_j = \sum_{k=0}^{n} l_{jk}x_k$$

Writing the expanded form of this equation in matrix notation, we have

$$\begin{vmatrix} j_0 \\ j_1 \\ j_2 \\ j_3 \\ j_4 \\ j_i \end{vmatrix} = \begin{vmatrix} l_{00} & l_{01} & l_{02} & l_{03} & l_{04} & l_{0i} \\ l_{10} & l_{11} & l_{12} & l_{13} & l_{14} & l_{1i} \\ l_{20} & l_{21} & l_{22} & l_{23} & l_{24} & l_{2i} \\ l_{30} & l_{31} & l_{32} & l_{33} & l_{34} & l_{3i} \\ l_{40} & l_{41} & l_{42} & l_{43} & l_{44} & l_{4i} \\ l_{i0} & l_{i1} & l_{i2} & l_{i3} & l_{i4} & l_{ii} \end{vmatrix} \begin{vmatrix} x_0 \\ x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_i \end{vmatrix} \qquad (6.9)$$

and the equilibrium conditions are:

$$x_j = x_0 + jx_i \qquad (j=1,2,3,4) \qquad (6.10)$$

In addition, the total flows of cadmium, J_0 , and iodide, J_i , are related to the flows of the complex species containing these ions, thus

$$J_0 = \sum_{k=0}^{4} j_k \quad (k\neq i) \qquad J_i = \sum_{k=1}^{4} kj_k + j_i \qquad (6.11)$$

Using equations (6.9),(6.10), and (6.11), the L_{jk} (j,k=1,2) of the binary solution may be related to the l_{jk} (j,k=0,1,2,3,4,i) of the individual species, giving equations (6.12a-c)..

$$L_{11}(=L_{00}) = \begin{vmatrix} l_{00} & l_{01} & l_{02} & l_{03} & l_{04} \\ l_{10} & l_{11} & l_{12} & l_{13} & l_{14} \\ l_{20} & l_{21} & l_{22} & l_{23} & l_{24} \\ l_{30} & l_{31} & l_{32} & l_{33} & l_{34} \\ l_{40} & l_{41} & l_{42} & l_{43} & l_{44} \end{vmatrix} \qquad (6.12a)$$

$$L_{12} = L_{21}(=L_{0i}) = \begin{vmatrix} l_{01} & 2l_{02} & 3l_{03} & 4l_{04} & l_{0i} \\ l_{11} & 2l_{12} & 3l_{13} & 4l_{14} & l_{1i} \\ l_{21} & 2l_{22} & 3l_{23} & 4l_{24} & l_{2i} \\ l_{31} & 2l_{32} & 3l_{33} & 4l_{34} & l_{3i} \\ l_{41} & 2l_{42} & 3l_{43} & 4l_{44} & l_{4i} \end{vmatrix} \qquad (6.12b)$$

$$L_{22}(=L_{ii}) = \begin{vmatrix} l_{11} & 2l_{12} & 3l_{13} & 4l_{14} & l_{1i} \\ 2l_{21} & 4l_{22} & 6l_{23} & 8l_{24} & 2l_{2i} \\ 3l_{31} & 6l_{32} & 9l_{33} & 12l_{34} & 3l_{3i} \\ 4l_{41} & 8l_{42} & 12l_{43} & 16l_{44} & 4l_{4i} \\ l_{i1} & 2l_{i2} & 3l_{i3} & 4l_{i4} & l_{ii} \end{vmatrix} \qquad (6.12c)$$

Using the concentrations of each species at particular bulk salt concentrations given in Table (6.10), Pikal's [142] limiting law expression (equation (4.7)) was used to calculate the l_{jk} of equations (6.12).

Pikal's expression describes only ionic inter-

TM	CD	CDI	CDI2	CDI3	CDI4	I	MU*
0.000100	0.000097	0.000003	0.000000	0.000000	0.000000	0.000197	0.000294
0.000200	0.000188	0.000013	0.000000	0.000000	0.000000	0.000387	0.000575
0.000300	0.000273	0.000026	0.000001	0.000000	0.000000	0.000573	0.000847
0.000400	0.000355	0.000044	0.000001	0.000000	0.000000	0.000754	0.001109
0.000501	0.000433	0.000065	0.000002	0.000000	0.000000	0.000931	0.001364
0.000601	0.000507	0.000090	0.000004	0.000000	0.000000	0.001103	0.001611
0.000701	0.000579	0.000117	0.000005	0.000000	0.000000	0.001273	0.001852
0.000801	0.000647	0.000146	0.000008	0.000000	0.000000	0.001439	0.002088
0.000901	0.000713	0.000177	0.000010	0.000000	0.000000	0.001603	0.002317
0.001001	0.000777	0.000210	0.000013	0.000000	0.000000	0.001763	0.002542
0.002005	0.001321	0.000612	0.000069	0.000003	0.000000	0.003246	0.004574
0.003013	0.001749	0.001086	0.000168	0.000010	0.000000	0.004561	0.006334
0.004025	0.002107	0.001590	0.000306	0.000023	0.000000	0.005755	0.007909
0.005018	0.002406	0.002098	0.000471	0.000042	0.000000	0.006851	0.009318
0.006020	0.002674	0.002612	0.000666	0.000068	0.000000	0.007872	0.010634
0.007019	0.002913	0.003123	0.000881	0.000101	0.000000	0.008829	0.011862
0.008023	0.003133	0.003629	0.001119	0.000142	0.000000	0.009730	0.013027
0.009026	0.003335	0.004128	0.001373	0.000190	0.000000	0.010583	0.014133
0.010029	0.003523	0.004620	0.001642	0.000244	0.000000	0.011393	0.015189
0.019995	0.005047	0.009019	0.004580	0.001039	0.000310	0.017459	0.024469
0.029998	0.006310	0.012881	0.007779	0.002187	0.000841	0.021632	0.032651
0.040000	0.007515	0.016414	0.010953	0.003521	0.001589	0.024726	0.040556
0.049995	0.008718	0.019754	0.014033	0.004953	0.002537	0.027168	0.048445
0.059995	0.009944	0.022957	0.017022	0.006445	0.003628	0.029147	0.056416
0.069996	0.011198	0.026068	0.019915	0.007969	0.004846	0.030807	0.064508
0.080002	0.012490	0.029079	0.022737	0.009519	0.006178	0.032181	0.072726
0.089999	0.013807	0.032089	0.025448	0.011062	0.007593	0.033455	0.081104
0.100000	0.015161	0.035032	0.028097	0.012614	0.009095	0.034550	0.089611

Table (6.10) Concentrations of each species at various bulk salt concentrations.

* Ionic Strength.

TM	CD	CDI	CDI2	CDI3	CDI4	I	MU
0.149994	0.022386	0.049304	0.040447	0.020303	0.017555	0.038660	0.134086
0.199942	0.030250	0.063161	0.051593	0.027786	0.027151	0.041538	0.181267
0.249930	0.038584	0.076783	0.061925	0.035146	0.037492	0.043774	0.230227
0.299927	0.047256	0.090265	0.071657	0.042403	0.048346	0.045631	0.280643
0.349843	0.056121	0.103681	0.080983	0.049530	0.059528	0.047223	0.331305
0.400163	0.065157	0.117093	0.089971	0.056979	0.070956	0.048643	0.383021
0.699715	0.119127	0.199015	0.140457	0.100358	0.140756	0.055161	0.698305
0.800046	0.136225	0.227380	0.156967	0.115924	0.163549	0.056846	0.799615
0.899597	0.152649	0.256391	0.173483	0.131213	0.185862	0.058405	0.900231
0.999958	0.168348	0.286123	0.190147	0.147743	0.207597	0.059845	0.998766

Table (6.10) continued.

actions, consequently no estimate is available for the l_{2j} (j=0,1,2,3,4,i) representing interactions between the neutral species CdI_2 and other species.

In these calculations, the values for λ_1^0, λ_3^0, and λ_4^0 (the equivalent conductances at infinite dilution of species CdI^+, CdI_3^-, and CdI_4^{2-}) were 'guessed', that is assigned certain values within the range 40-100 conductance units. The 'guesses' for λ_3^0 and λ_4^0 were influenced by the general premise that anionic λ^0 values increase with increasing negative charge. Allowing for the uncertainty in the value of λ_0^0 ($\lambda_{Cd}^{0}{}_{2+}$) obtained in this work, calculations were performed using the value of Garland et al.[37] of 53.0 ohm cm^2/equiv. as well as our own estimate of 58.9 ohm cm^2/equiv.

Several calculations were performed for each of several different bulk salt concentrations, using various 'guesses' for λ_1^0, λ_3^0, and λ_4^0. The (calculated) l_{jk} obtained in this way were substituted in equations (6.12), giving values for L_{jk}. These calculated values are compared with observed in Table (6.11). Also given in this Table are the assigned values for λ_0^0, λ_1^0, λ_3^0, and λ_4^0. Robinson and Stokes'[155] value was used for $\lambda_{I^-}^0$.

In estimating L_{11}/N, runs 4 and 5 give the best correlation with the observed values, whilst runs 1,2, and 3 consistently overestimate the true value. Runs 4 and 5 again give the closest correlation in estimating L_{12}/N and runs 1,2, and 3 again overestimate the true value. In estimating L_{22}/N, however, runs 1,2, and 3 give the best results, whereas runs 4 and 5 seriously underestimate the true value, particularly at higher concentrations.

In assessing the validity of the calculations, it should be noted that, in general, Pikal's limiting law expression tends to overestimate the cross coefficients l_{jk} (j,k=0,1,2,3,4,i;j≠k) whilst underestimating the direct coefficients l_{jj} (j=0,1,2,3,4,i).[142] Accordingly, to aid the assessment of the data, the quantities Λ, equivalent conductance, D, diffusion coefficient, and t_i, transport number, were calculated using equations (2.29), (2.44), and (2.35), and compared with their measured

Table (6.11) Observed and calculated values of L_{ij}/N for CdI_2.

L_{11}/N ($x10^{12}$)

Conc. (N)	Obs.	run 1	2	3	4	5
0.0	1.581	-	-	-	-	-
0.01	1.432	1.998	1.798	1.801	1.646	1.426
0.02	1.464	1.805	1.807	1.816	1.600	1.358
0.1	1.515	1.756	1.782	1.817	1.512	1.289
0.2	1.556	1.778	1.828	1.812	1.558	1.344

L_{12}/N ($x10^{12}$)

Conc. (N)	Obs.	run 1	2	3	4	5
0.0	0.000	-.	-	-	-	-
0.01	1.131	1.555	1.557	1.566	1.317	1.096
0.02	1.528	1.854	1.862	1.888	1.556	1.309
0.1	2.430	2.729	2.827	2.930	2.347	2.069
0.2	2.803	3.133	3.307	3.435	2.788	2.481

L_{22}/N ($x10^{12}$)

Conc. (N)	Obs.	run 1	2	3	4	5
0.0	8.249	-	-	-	-	-
0.01	6.837	7.077	7.083	7.109	6.789	6.559
0.02	6.984	6.765	6.797	6.878	6.344	6.072
0.1	7.533	7.186	7.549	7.856	6.514	6.029
0.2	8.033	7.283	7.911	8.294	6.709	6.056

Table (6.11) continued

Assigned values for λ_i^0 (i=0,1,3,4,i).

	run				
	1	2	3	4	5
λ_0^0	53.0	59.0	59.0	58.9	58.9
λ_1^0	60.0	60.0	60.0	50.0	40.0
λ_3^0	60.0	60.0	67.0	40.0	40.0
λ_4^0	60.0	80.0	80.0	85.0	70.0
λ_i^0	76.8	76.8	76.8	76.8	76.8

values. The results are given in Table (6.12).

Equivalent conductance , Λ, is taken as the most valid quantity for evaluation of the calculations, since terms involving l_{2j} (j=0,1,2,3,4,i) cancel in the expression for Λ , thus eliminating one source of error. Additionally, in view of the fact that Pikal's equation is a limiting law expression, the most valid region for comparison of calculated and observed data is within the concentration range 0-0.1N.

On this basis, runs 1,2, and 3 give better estimates for Λ than runs 4 and 5, possibly because any overestimate for L_{11}/N and L_{12}/N is compensated by the underestimate for L_{22}/N. Runs 4 and 5 also overestimate L_{11}/N and L_{12}/N, though to a far lesser extent, whilst seriously underestimating L_{22}/N, so one would expect to observe a low estimate for Λ , which is in fact the case.

For the other transport quantities, D is in general overestimated by runs 1,2,3, and 5, though run 4 yields results in good agreement with the observed values. Transport numbers are also overestimated , by all five runs, though in this case run 5 gives the best correlation, within approximately 10% at 0.1N.

In general, however, agreement between calculated and observed D, t_i, and Λ is surprisingly good up to a concentration of 0.1N.

Although the theoretical equations presented above are semi-quantitative only in dilute solutions of cadmium iodide, it seems likely that the qualitative aspects have some validity in any system in which complexing of this type occurs.

Table (6.12) Observed and calculated values for , D , and t_i for CdI_2.

$\Lambda = 9.3109.10^{12}(4L_{11}/N + L_{22}/N - 4L_{12}/N)$.

Conc. (N)	D Obs.	run 1	2	3	4	5
0.0		-	-	-	-	-
0.01	74.86	74.92	74.94	74.96	75.47	73.35
0.02	62.63	61.17	61.24	61.29	60.70	58.34
0.1	36.06	30.64	31.40	31.72	29.58	27.07
0.2	28.36	17.34	18.59	19.00	16.65	14.03

$t_i = (4L_{11}/N - 2L_{12}/N)/ \alpha'$

Conc. (N)	D Obs.	run 1	2	3	4	5
0.0		-	-	-	-	-
0.01	0.431	0.507	0.507	0.506	0.487	0.446
0.02	0.416	0.535	0.542	0.530	0.504	0.449
0.1	0.310	0.475	0.438	0.414	0.427	0.350
0.2	0.203	0.454	0.350	0.302	0.367	0.274

$= 14.8734.10^{6}(L_{11}/N.L_{22}/N - (L_{12}/N)^2)/ \alpha'$

Conc. (N)	D Obs.	run 1	2	3	4	5
0.0		-	-	-	-	-
0.01	1.187	1.434	1.437	1.442	1.306	1.146
0.02	1.076	1.226	1.230	1.243	1.088	0.956
0.1	0.806	0.890	0.919	0.947	0.775	0.680
0.2	0.780	0.861	0.904	0.934	0.767	0.673

$\alpha' = (4L_{11}/N + L_{22}/N - 4L_{12}/N)$.

APPENDIX 1

CURVE-FIT DATA

Salt	Y	X	a_0	a_1	a_2	a_3
LiCl	lnc	lnk'	-4.6776	1.0317	0.0065818	0.00072866
NaCl	"	"	-4.77964	1.02802	0.0058551	0.00065172
KCl	"	"	04.95916	1.02152	0.0074681	-0.00024766
RbCl	"	"	-4.9861	1.0227	0.0068655	-0.00015673
CsCl	c	k'	$-2.5718.10^{-4}$	$6.9911.10^{-5}$	$6.9085.10^{-5}$	$-1.3626.10^{-6}$

k' = 10^3x specific conductivity.

Appendix (1a) Coefficients of the equation $Y = \sum_{i=0}^{3} a_i X^i$ between concentration and specific conductivity for the alkali chlorides.

Salt	Y	X	a_0	a_1	a_2	a_3
LiCl	$\ln\Lambda$	$\ln c$	4.3365	-0.13132	-0.016395	-0.00093181
NaCl	"	"	4.46486	-0.11861	-0.014366	-0.00076412
KCl	"	"	4.71746	-0.069961	-0.0030170	+0.00025442
RbCl	"	"	4.7413	-0.070856	-0.0033057	+0.00021576
CsCl	Λ	c	148.00	-395.77	3785.9	-15520.0

Appendix (1b) Coefficients of the equation $Y = \sum_{i=0}^{3} a_i X^i$ between concentration and equivalent conductivity for the alkali chlorides.

Salt	Y	X	a_0	a_1	a_2
LiCl	m/c	c	1.002795	0.017994	0.00096856
	c/m	m	0.99271	-0.017857	-0.0002906
NaCl	m/c	c	1.002165	0.019765	0.0002006
	c/m	m	0.99783	-0.019529	0.0003907
KCl	m/c	c	1.0031	0.028	0.0018
	c/m	m	0.997	-0.0284	0.0003
RbCl	m/c	c	1.0031	0.0324	0.0026
	c/m	m	0.997	-0.0331	0.0004
CsCl	m/c	c	1.0032	0.039	0.0035
	c/m	m	0.997	-0.040	0.0008

Appendix (1c) Coefficients of the density equations for the alkali chlorides.

Salt	Y	X	a_0	a_1	a_2	a_3	a_4	a_5
LiCl	$10^5 D_{11}$	c	0.97344	-0.056317	0.0018282	-	-	-
	$10^5 D_{22}$	c	1.96581	-0.27941	-0.086843	0.12416	-0.045534	0.0052897
	$10^5 D_{00}$	c	2.19039	-0.25052	0.016947	-	-	-
NaCl	$10^5 D_{11}$	c	1.31383	-0.084690	-0.0027983	-	-	-
	$10^5 D_{22}$	c	1.97286	-0.24490	0.045165	-0.0071067	-	-
	$10^5 D_{00}$	c	2.20746	-0.085814	-0.021937	-	-	-
KCl	$10^5 D_{11}$	c	1.91953	-0.085146	0.0203795	-	-	-
	$10^5 D_{22}$	c	1.96300	0.024037	-0.034932	0.0042434	-	-
	$10^5 D_{00}$	c	2.21525	0.10196	-0.034165	-	-	-
RbCl	$10^5 D_{11}$	c	-	-	-	-	-	-
	$10^5 D_{22}$	c	1.96730	-0.029556	0.003348	-	-	-
	$10^5 D_{00}$	c	2.23081	0.12019	-0.023442	-	-	-
CsCl	$10^5 D_{11}$	c	1.95551	-0.016238	-0.0043274	-	-	-
	$10^5 D_{22}$	c	1.99270	-0.14728	0.14155	-0.023532	-	-
	$10^5 D_{00}$	c	2.21280	0.16430	-0.039688	-	-	-

Appendix (1d) Coefficients of the equation $Y = \sum_{i=0}^{5} a_i X^i$ for the alkali chlorides.

Appendix (1e) Coefficients of the equations between lnf and m, and between lnf and lnm, for CdI_2.

$$\log f = -0.0027871 - 4.82285m^{\frac{1}{2}} + 7.47439m - 6.72163m^{3/2} + 2.50781m^2$$

$$\log f = -1.58101 - 0.45507\ (\log m) + 0.2975\ (\log m)^2 + 0.16034\ (\log m)^3 + 0.021593\ (\log m)^4$$

Appendix (1f) Coefficients of th e equation between transport number (t_2) and molality for CdI_2.

$$t_2 = o.55373 + 3.0554m - 7.5121m^2 + 12.0803m^3 - 9.3962m^4 + 2.7748m^5.$$

APPENDIX 2

COMPUTER PROGRAMMES

Programme 1 This programme calculates concentration from measured specific conductances and the weights of solution before and after dilution. The relevant curve-fit equations are applicable only at concentrations <0.1M. The original concentration of the undiluted solution is calculated from these weights.

```
begin comment Adaptation of programme 3 of Jalotas thesis for
the calculation of concentration by the conductometric method
of analysis;
integer i,n,f,l,j,g,r; real k,wb,wx,wy,C,m,wg,lamda,st;
open(2C); open(7C); copytext(2C,7C,[;]);
f:=format([-nd.dddsddddsdddc]);again: l:=read(2C);
if l=C then goto fin;n:=read(2C); k:=read(2C);
begin array a,b[1:n];
for i:=1 step 1 until n do a[i]:=read(2C);
for i:=1 step 1 until n do b[i]:=read(2C);
 C:=C.C;k:=ln(k); for i:=1 step 1 until n do
 C:=C+a[i]×k↑(i-1); rep:st:=C; lamda:=C.C;
for i:=1 step 1 until n do lamda:=lamda+b[i]×C↑(i-1);
C:=k-lamda; if abs((exp(st)-exp(C))/exp(C))>C.CCC3
then goto rep else begin if abs((st-C)/C)>C.CCC3
then goto rep end; r:=read(2C);
if r= 1 then goto calc else begin C:=exp(C);
 copytext(2C,7C,[:]); goto check ; end;
calc:g:=read(2C); begin array p,q[1:g];
 C:=exp(C); wb:=read(2C);
for j:=1 step 1 until g do p[j]:=read(2C);
for j:=1 step 1 until g do q[j]:=read(2C);
copytext(2C,7C,[:]);wx:=read(2C); wy:=read(2C); m:=C.C;
for j:=1 step 1 until g do m:=m+ p[j]×C↑(j-1);
m:=m×C; wg:= m×wb×wy/(1CCC+m×wb);
m:=wg×1CCC/(wb×(wx-wg)); C:=C.C;
for j:=1 step 1 until g do C:=C+q[j]×m↑(j-1);
C:=m×C; end; end; check:  writetext(7C,[CONCENTRATION*=*]);
 write(7C,f,C); goto again;
fin: close(2C); close(7C); end→
```

Programme 2 This programme calculates the cell constant of a diffusion cell from specific conductance data provided by cell calibration experiments using potassium chloride solutions. The programme may also be used to calculate the integral diffusion coefficient of any salt from the relevant data.

```
begin  comment This program calculates concentrations
for a diffusion run by the conuctometric method of analysis,
calibrates the cell for cell constant with a standard salt
and then calculates the integral diffusion coefficient for an
unknown salt;
integer l,n,i,f,j,r,s;
real v,k,t,C1,C2,C3,C4,c,di,dma,dmb,cma,cmb,ci,wx,wy,wb,wg,m;
open(2C);    open(7C);
copytext(2C,7C, [;]);f:= format([ -nddd.ddddddc]);
again:    n:= read(2C);    r:= read(2C);
begin array a, b[1:n], p,q[1:3];

real procedure C(k);value k;real k;begin  real st,lamda, CC;
CC:=C.C;  if r=6 then k:=ln(k); for i:=1 step 1 until n do
CC:= CC+ a[i]xk↑(i-1); rep: st:=CC;        lamda:= C.C;
for i:=1 step 1 until n do  lamda:= lamda+ b[i]xCC↑(i-1);
if r=6 then CC:=k-lamda else CC := k/lamda;
if r=6 then begin if abs((exp(st)-exp(CC))/exp(CC))
>C.CCC3 then goto rep  end else   begin
if abs((st-CC)/CC) > C.CCC3 then goto rep  end;
if r=6 then CC := exp(CC);     if s=15 then  begin  m:= C.C;
for j:= 1 step 1 until  3 do    m:= m + p[j]xCC↑(j-1);
m:= mxCC;  wg := mxwbxwy/(1CCC+mxwb);
m := wgx1CCC/(wbx(wx-wg));
CC:=C.C; for j:= 1  step 1 until 3 do CC:= CC+ q[j]xm↑(j-1);
CC := mxCC        end;       C:= CC   end C;

real procedure d(c); value c; real c;  begin
if c≤.C1 then d:= 1.9834 - 1C.4C36xc+ 978.6C2xc↑2-3922C.CxC↑3;
if c>.C1 and c≤.1 then d:= 1.959C - 2.41C1xc + 27.3377xc↑2
 - 118.482xc↑3;
if c>.1 and c≤.5 then d:= 1.9C175 -C.36375xc  + C.825xc↑2
 -C.625xc↑3;
if c>.5 and c<3.9 then d:=  1.84273 +C.CCC36C167xc +C.C186942
xc↑2 -C.CC21745xc↑3; end d;


for i:= 1 step 1 until n do   a[i] := read(2C);
for i:= 1 step 1 until n do   b[i] := read(2C);
s:= read(2C); if s=15 then begin
wb:=read(2C);  for j:= 1 step 1 until 3 do p[j]:=read(2C);
for j:= 1 step 1 until 3 do q[j]:=read(2C);  end;

repeat:    copytext(2C, 7C, [:]);   v:=read(2C);
  s:= read(2C); if s=15 then begin wx:=read(2C);
 wy:=read(2C) end;
k:= read(2C); if k= C.C then C2:=C.C else C2 := C(k);

s:= read(2C); if s=15 then begin  wx:=read(2C);
 wy:=read(2C) end; k:= read(2C); C3:= C(k);
s:=read(2C);  if s=15 then begin  wx:=read(2C);

 wy:=read(2C) end;k:= read(2C);   C4:= C(k);

t:=read(2C);   l:=read(2C); C1:= C3+ (C4-C2)xv;
cma:= (C1+C3)/2;    cmb:= (C2+C4)/2;
```

```
writetext(7C, [ cma*= ]);   write(7C, f, cma);
writetext(7C, [ cmb*= ]);   write(7C, f, cmb);
writetext(7C, [ C1*= ] );   write(7C, f, C1 );
writetext(7C, [ C2*= ] );   write(7C, f, C2 );
writetext(7C, [ C3*= ] );   write(7C, f, C3 );
writetext(7C, [ C4*= ] );   write(7C, f, C4 );
writetext(7C, [ C1-C2*=*]);  write(7C, f, C1-C2);
writetext(7C,[ C3-C4*=*]);   write(7C, f, C3-C4);

ci:=(C1-C2)/(C3-C4);  writetext(7C, [C1-C2/C3-C4 *=* ] );
write(7C, f, ci );
writetext( 7C, [betaxdo *=* ]);   write(7C, f, ln(ci)x10.5/t);

if l=7 then  begin c:= cma; dma:= d(c);
writetext(7C, [dma*=*]); write(7C, f, dma);
c:=cmb; dmb:= d(c); writetext(7C, [dmb*=*]);
write(7C, f, dmb);
di:= (cmaxdma-cmbxdmb)/(cma-cmb); writetext(7C, [d@i*=*]);
write(7C, f, di);  writetext(7C, [beta*=*]);
write(7C, f, ln(ci)x10.5/(txdi) ); end;  l:= read(2C);
if l=1 then goto repeat else if l=2 then goto again  end;
close(2C);    close(7C);      end→
```

Programme 3 This programme calculates transport numbers according to the method of Rutledge.[157]

```
begincomment this program works out differentials by the method
             of rutledge from the coefficients of the curve fit
             equation between x and y;

        real xstart, xfin, h , no, conc;
        integer i, j, k, n, f1, f2, f3, m, l, p, f4, f5;

        realarray b[0:5];
        open(20); open(70);

        p:=read(20);
        if p=0 then goto redo;
        l:= read(20);
        for i:= 0 step 1 until l do b[i]:=read(20);
        for i:=l+1 step 1 until 5 do b[i]:=0;

redo:   begin
         array a[0:5], x[-3:2], y[-2:2];
        copytext(20,70,[;;]); k:=read(20);
        for i:=0step 1 until k do  a[i]:=read(20);
        for i:=k+1 step 1until 5 do  a[i]:= 0;

moredo:xstart:=read(20); xfin:=read(20); h:=read(20);

        no:=abs((xstart - xfin)/h);
        n:=entier(no);

begin   array r[1:n]                    f1:=format([4s-nd.dddd]);
        x[-3]:=xstar                    f2:=format([3s-nd.dddd]);
        for j:=2 ste                    f3:=format([3s-nd.ddddddc]);
begin   for i:=-2 step 1 until 2 do
        beginx[i]:=x[i-1] + h;
              y[i]:=a[0]+x[i]x(a[1]+x[i]x(a[2]+x[i]x(a[3]+
                                  x[i]x(a[4]+x[i]xa[5]))));
        end;

        x[-3]:=x[-2];
        t[j-1]:=(-3xy[-2]-10xy[-1]+18xy[0]-6xy[1]+y[2])/(12xh);
        r[j]:=(y[-2]-8xy[-1]+8xy[1]-y[2])/(12xh);
        s[j+1]:=(-y[-2]+6xy[-1]-18xy[0]+10xy[1]+3xy[2])/(12xh);

        E[j-1]:=x[-1];  E[j]:=x[0];  E[j+1]:=x[1];
end;

        r[1]:=t[1]; s[1]:=t[1]; s[2]:=(t[2]+r[2])/2;
        t[j+1]:=r[j+1]:=s[j+1];  t[j]:=(s[j]+r[j])/2;

        f1:=format([4s-nd.dddd]);
        f2:=format([3s-nd.dddd]);
        f3:=format([3s-nd.ddddddc]);

        f4:=format([3s-nd.ddddddc]);
        f5:=format([3s-nd.dddddd]);

        if p=1 thengoto altern;
  writetext(70,[[cc6s]DERIV*1[4s]DERIV*2[4s]DERIV*3[4s]
                          AVERAGE[6s]X*VALUE[cc]]);
```

```
        for i:=1step 1 until j+1do
        begin write(7C,f1,t[i]);
              write(7C,f2,r[i]);
              write(7C,f2,s[i]);
              write(7C,f2,(t[i]+r[i]+s[i])/3);
              write(7C,f3,E[i]);
        end;
        goto next;

altern:writetext(7C,[[cc6s]DERIV*1[4s]DERIV*2[4s]DERIV*3[4s]
                     AVERAGE[5s]DELTA*E[6s]MOLARITY[cc]]);

        for i:=1 step 1 until j+1 do
        begin conc:=b[C]+E[i]×(b[1]+E[i]×(b[2]+E[i]×(b[3]+E[i]
                          ×(b[4]+E[i]×b[5]))));
              write(7C,f1,t[i]);
              write(7C,f2,r[i]);
              write(7C,f2,s[i]);
              write(7C,f2,(t[i]+r[i]+s[i])/3);
              write(7C,f5,E[i]);
              write(7C,f4,conc);
        end;
next:   end;
          m:=read(2C);
        if m=1 then goto redo;
        if m=2 then goto moredo;
                end; close(2C); close(7C);
end→
```

Programme 4 This programme calculates the phenomenological coefficients L_{ij} and R_{ij} from the experimentally-measured transport parameters D, Ɛ, and Λ, printing the results in tabular form.

```
begin   comment This program reads n sets of concn,
        molality/density, eqivalent conductivity,
        transport numbers, diffusion coefficients
        and activity term and it then calculates
        Onsager L and R coefficients and three degrees
        of coupling and outputs the results in tabular
        form;
           integer r, r1, r2, n, z, z1, z2, f, md, i, DV;
      real    R, F, T, M, q;

open(20);        DV:=read(20);          open(DV);
 f:=format([-nddd.dddd]); copytext(20, DV, [;;]);
repeat: R:=read(20);  F:=read(20);  T:=read(20);
again:  copytext(20, DV, [:]);
        M:=read(20);  r1:=read(20);  r2:=read(20);
 z1:=read(20);          z2:=read(20);  r:=r1+r2;
   z:=read(20);  n:=read(20);  md:=read(20);
begin array c, d, m, t1, lda, D, l11, l22, l12, R11,
      R22, R12, R10, R20, R00, F12, x, y, act [1:n];
for i:= 1 step 1 until n do begin
c[i]:=read(20);   d[i]:=read(20); lda[i]:=read(20);
t1[i]:=read(20);   D[i]:=read(20);   act[i]:=read(20)
end;
q:=10↑8×R×T×r×r1×z1;
for i := 1 step 1 until n do  begin
x[i]:=D[i]/(q×act[i]);  y[i]:=lda[i]/(1000×F↑2);
if md = 3 then m[i] := d[i] else
 m[i]:=c[i]/(d[i]-0.001×c[i]×M);

l11[i]:=y[i]×t1[i]↑2/z1↑2+r1↑2×x[i];
if c[i]=0.0 then l12[i]:=0.0 else
 l12[i]:=y[i]×t1[i]×(1-t1[i])/(z1×z2) + r1×r2×x[i];
l22[i]:=y[i]×(1-t1[i])↑2/z2↑2+r2↑2×x[i];
x[i]:=l11[i]×l22[i]-l12[i]↑2;
R11[i]:=l22[i]/x[i];
R12[i]:=-l12[i]/x[i];   F12[i]:=-R12[i]×y[i];
R22[i]:=l11[i]/x[i];
if md = 3 then  begin  if c[i] = 0.0 then x[i] :=0.01807/z
 else x[i] := 18.015×m[i]/( 1000 × z × c[i]) end
           else   x[i]:= 18.015/(z×(1000×d[i]-M×c[i]));
R10[i]:=-(r1×R11[i]+r2×R12[i])×x[i];
R20[i]:=-(r1×R12[i]+r2×R22[i])×x[i];
R00[i]:=-(r1×R10[i]+r2×R20[i])×x[i]    end;     test(0);

writetext(DV, [ [11s]c[8s]m[7s]Eqv*Cond[6s]t+[5s]D(v)₁₀5[s]
                        1+m×dlnGama/dm[2c] ]);
for i:=1 step 1 until n do begin
space(DV, 5);
 write(DV, f, c[i] );
  write(DV, format([ndd.dddddd]), m[i]);
   write(DV, format([-ssnddd.dd]), lda[i]);
    write(DV, f, t1[i]);
     write(DV, f, D[i]);
      write(DV, f, act[i]); newline(DV, 1); end;
```

```
writetext( DV, [ [2c9s]Sqrt*S[4s]111/N[5s]112/N
          [5s]122/N[6s]F12[7s]Q12[c10s]
          ×10[7s]₁₀+12[6s]₁₀+12[6s]₁₀+12[2c] ] );

for i := 1 step 1 until n do begin

space(DV, 5);
 write(DV, f, 10xsqrt( z x c[i] x ( z1 - z2 )/2) );
  write(DV, f, 111[i] x ₁₀12 );
   write(DV, f, 112[i]x₁₀12 );
    write(DV, f, 122[i]x₁₀12 );
     write(DV, f, F12[i]);
      write(DV, f, 112[i]/ sqrt( 111[i]x122[i] ) );
       newline(DV, 1);  end;

writetext( DV, [ [2c9s]Sqrt*S[4s]NR11[6s]-NR12[5s]
          NR22[7s] Q10[7s]Q20[c10s]x10[6s]₁₀-11
         [7s]₁₀-11  [5s]₁₀-11[2c] ] );

for i := 1 step 1 until n do begin


space(DV,5);
 write(DV, f, 1( x sqrt( z x c[i] x (z1-z2)/2 ) );
  write(DV, f, R11[i]x₁₀-11);
   write(DV, f, -R12[i]x₁₀-11);
    write(DV, f,  R22[i]x₁₀-11);
     write(DV, f, -R10[i]/sqrt( R11[i]xR00[i] ) );
      write(DV, f, -R20[i]/sqrt(R22[i]xR00[i]) );
       newline(DV, 1);  end;



writetext( DV, [ [2c9s]Sqrt*S[4s]-R10[6s]
-R20[6s]-COR10[4s]-COR20[4s]R00/N[c10s]
  x10[7s]₁₀-9[7s]₁₀-9[6s]₁₀-11[6s]₁₀-11[8s]₁₀-7[2c] ] );

for i:= 1 step 1 until n do begin


space(DV,5);
 write(DV, f, 10x sqrt( zx c[i] x (z1-z2)/2 ) );
  write(DV, f, -₁₀-9xR10[i] );  write(DV, f, -₁₀-9xR20[i] );
   write(DV, f, -₁₀-11 xR10[i]/(zx x[i]) );
    write(DV, f, -₁₀-11 x R20[i]/ (zxx[i]) );
     write(DV, f, R00[i]x₁₀-7 );  newline(DV, 1);
end   end;       n:=read(20);
if n = 1 then goto again else if n=2 then goto repeat;
close(20);   close(DV);
end→
```

REFERENCES

1 Adamson A.W. J.Chem.Phys. 15 762 (1947).

2 Adamson A.W.,Cobble J.W., Neilsen J.M. J.Chem.Phys. 17 740 (1949).

3 Adamson A.W., Irani R.R. J.Amer.Chem.Soc. 79 2967 (1957).

4 Anderson J.S., Saddington K. J.Chem.Soc. S381 (1949).

5 Andreev G.A. Russ.J.Phys.Chem. 36 835 (1963).

6 Barnes C. Physics 5 4 (1934).

7 Bates R.G., Vosburgh W.C. J.Amer.Chem.Soc. 59 1583 (1937).

8 Bates R.G., Vosburgh W.C. ibid. 60 137 (1938).

9 Bates R.G. ibid. 63 399 (1941).

10 Bearman R.J. J.Phys.Chem. 66 2072 (1962).

11 Bevilacqua E.M., Bevilacqua E.B., Bender M.M., Williams J.W. Ann.N.Y.Acad.Sci. 46 309 (1945).

12 Bogdan P. Z.Physik.Chem. 37 700 (1901).

13 Bray G.A. Anal.Biochem. 1 279 (1960).

14 Brun B. Ph.D. Thesis, Montpellier, France,1967.

15 Brun B., Salvinien J., Servent M. Compte Rendus Acad.Sci.Ser.C 269 1 (1969).

16 Bryngdahl O. Acta chem.Scand. 11 1017 (1957).

17 Carr H.Y., Purcell E.M. Phys.Rev. 94 630 (1954).

18 Chapman T.W., Newman J. 'Compilation of selected thermodynamic and transport properties of binary electrolytes in aqueous solution.' University of California, UCRL 17767, 1967.

19 Chapman T.W. Ph.D. Thesis, University of California, UCRL 17768, 1968.

20 Clack B.W. Proc.Phys.Soc. 36 313 (1924).

21 Coulson C.A., Cox J.T., Ogston A.G., Philpot J.St.L. Proc.Roy.Soc. 192A 382 (1948).

22 Cox W.M., Wolfenden J.H. ibid. 145A 475 (1934).

23 Cuddleback R.B., Koeller R.C., Drickamer H.G. J.Chem.Phys. 21 589 (1953).

24 Cussler E.L., Dunlop P.J. J.Phys.Chem. 70 1880 (1966).

25 Das T.P., Saha A.K. Phys.Rev. 93 749 (1954).

26 Devell L. Acta chem. Scand. 16 2177 (1962).
27 Douglass D.C., McCall D.W. J.Phys.Chem. 62 1102 (1958).
28 Douglass D.C., McCall D.W. J.Chem.Phys. 31 569 (1959).
29 Dunsmore H.S., Jalota S.K., Paterson R. J.Chem.Soc. A 1061 (1969).
30 Emel'yanov M.I. J.Struct.Chem. 6 270 (1965).
31 Emel'yanov M.I., Nikiforov E.A., Kucheryavenko N.S. J.Struct.Chem. 9 852 (1968).
32 Fell A. Ph.D. Thesis, University of Cambridge, 1965.
33 Fick A. Pogg.Ann. 94 59 (1855).
34 Francesconi R. Ing.Chim.Ital. 6 72 (1970).
35 Friedman A.M., Kennedy J.W. J.Amer.Chem.Soc. 77 4499 (1955).
36 Fujita H., Gosting L.J. J.Phys.Chem. 64 1256 (1960).
37 Garland C.W., Tong S., Stockmayer W.H. J.Phys.Chem. 69 1718 (1965).
38 Geddes A.L., Pontius R.B. 'Determination of Diffusivity' in 'Techniques of Organic Chemistry', Editor A.Weissberger, Physical Methods of Organic Chemistry, 3rd. edition, Interscience, N.Y.,1960.
39 Getman F.H. J.Phys.Chem. 32 940 (1928).
40 Gillen K.I., Douglass D.C., Hoch M.J.R. J.Chem.Phys. 57 5117 (1972).
41 Goncharov V.V., Yashkichev V.I., Markova V.G., Plekseeva L.S. Radiokhimiya 12 905 (1970).
42 Gordon A.R. Ann.N.Y.Acad.Sci. 46 285 (1945).
43 Gosting L.J., Hanson E.M., Kegeles G., Morris M.S. Rev.Sci.Instr. 20 209 (1949).
44 Gosting L.J. J.Amer.Chem.Soc. 72 4418 (1950).
45 Gosting L.J., Onsager L. ibid. 74 6066 (1952).
46 Gouy G.L. Compte Rend. 90 307 (1880).
47 Graupner K., Winter E.R.S. J.Chem.Soc. 1145 (1952).
48 de Groot S.R., Mazur P. 'Non-Equilibrium Thermodynamics', Interscience,N.Y.,1962. PP 31-34,57-64,308.
49 reference 48 PP 43-45.
50 Guggenheim E.A., Stokes R.H. Trans.Far.Soc. 54 1646 (1958).

51 Gurney R.W. 'Ionic Processes in Solution' McGraw-Hill,N.Y.,1953.

52 reference 51 p. 162.

53 Hafeman D.R. J.Phys.Chem. 69 4226 (1965).

54 Hahn E,L. Phys.Rev. 80 580 (1950).

55 Hamer W.J. J.Amer.Chem.Soc. 57 662 (1935).

56 Harned H.S.,French D.M. Ann.N.Y.Acad.Sci. 46 267 (1945).

57 Harned H.S.,Nuttall R.L., J.Amer.Chem.Soc. 69 736 (1947); ibid. 71 1460 (1949).

58 Harned H.S.,Gosting L.J. ibid. 73 159 (1951).

59 Harned H.S.,Owen B.B. 'The Physical Chemistry of Electrolyte Solutions', 3rd. Edition, Reinhold Publ. Corp., N.Y., 1958.

60 Hartley G.S.,Runnicles D.F. Proc.Roy.Soc 168A 401 (1938).

61 von Helmholtz H. Ann.Physik. 3 201 (1878).

62 Henrion P.N. Trans.Far.Soc. 60 75 (1964).

63 Hooyman G.J. Physica 22 751 (1956).

64 International Critical Tables Vols. 4-7.

65 Ives D.J.,Janz G.J. 'Reference Electrodes', Academic Press Inc., N.Y., 1961.

66 Jalota S.K. Ph.D. Thesis, Univ. of Glasgow, 1971.

67 Jalota S.K.,Paterson R. J.Chem.Soc.Far.Trans.1 69 1510 (1973).

68 Johnson P.A.,Babb.A.L. Chem.Revs. 56 387 (1956).

69 Jones G.,Josephs R.C. J.Amer.Chem.Soc. 50 1084 (1928).

70 Jones G.,Dole M. ibid. 51 2950 (1929).

71 Jones G.,Bollinger G.M. ibid. 53 411 (1931).

72 Jones G.,Bradshaw B.C. ibid, 55 1780 (1933).

73 Jones G.,Bollinger G.M. ibid. 57 280 (1935).

74 Jones J.R.,Rowlands D.L.G.,Monk C.B. Trans.Far.Soc. 61 1384 (1965).

75 Kaminsky M. Z.phys.Chem. 8 173 (1956).

76 Katchalsky A.,Curran P. 'Non-Equilibrium Thermodynamics in Biophysics', Harvard Univ. Press, Cambridge, 1965.

77 Kegeles G.,Gosting L.J. J.Amer.Chem.Soc. 69 2516 (1947).

78 Kim H. J.Phys.Chem. 70 562 (1966).

79 Kirkwood J.G.,Baldwin R.L.,Dunlop P.J.,Gosting L.J., Kegeles G. J.Chem.Phys. 33 1505 (1960).
80 Klemm A. Z.Naturforsch. 89 397 (1953).
81 Krauss C.J.,Spinks J.W.T. Can.J.Chem. 32 71 (1954).
82 Laity R.W. J.Chem.Phys. 30 682 (1959).
83 Laity R.W. J.Phys.Chem. 67 671 (1963).
84 Landolt-Barnstein 'Elektrische Eigenschaften', 6th. Edition, Springer-Verlag, Berlin,1960. p.260.
85 Leden I. Z.phys.Chem.(A) 188 160 (1941).
86 Lingane J.J.,Kolthoff I.M. J.Amer.Chem.Soc. 61 825 (1939).
87 Ljunggren S. Trans.Roy.Inst.Technol.Stockholm 172 1 (1961).
88 Lomgsworth L.G. Industr.Engng.Chem.(Anal.Ed.) 18 219 (1946).
89 Longsworth L.G. Ann.N.Y.Acad.Sci. 46 211 (1947).
90 Longsworth L.G. J.Amer.Chem.Soc. 69 2510 (1947).
91 Longsworth L.G. Rev.Sci.Instr. 21 524 (1950).
92 Longsworth L.G. J.Phys.Chem. 58 771 (1954).
93 Longsworth L.G. ibid. 63 80 (1959).
94 Longsworth L.G. ibid. 64 1914 (1960).
95 Macero D.J.,Rulfs C.L. J.Amer.Chem.Soc. 81 2942 (1959).
96 Marcinkowsky A.E.,Nelson F.,Krauss K.A. J.Phys.Chem. 69 303 (1965).
97 Marcinkowsky A.E.,Phillips H.O.,Krauss K.A. J.Phys.Chem. 69 3968 (1965).
98 Marcinkowsky A.E.,Phillips H.O.,Krauss K.A. J.Phys.Chem. 72 1201 (1968).
99 Marcinkowsky A.E.,Phillips H.O. J.Chem.Soc. A1 101 (1971).
100 Matyash I.V.,Toryanik A.I.,Yashkichev V.I. J.Struct.Chem. 5 713 (1964).
101 McBain J.W.,van Rysselberghe P.J.,Squance W.A. J.Phys.Chem. 35 999 (1931).
102 McBain J.W.,Dawson C.R. Proc.Roy.Soc. 148A 32 (1935).
103 McCall D.W.,Douglass D.C. J.Phys.Chem. 69 2001 (1965).
104 McCall D.W.,Douglass D.C. ibid. 71 987 (1967).
105 McGlaughlin E. Physica 26 650 (1960).
106 Micka K. Ber.Bunsenges.phys.chem. 72 60 (1968).
107 Miller D.G. Chem.Revs. 60 15 (1960).

108 Miller D.G. J.Phys.Chem. 70 2639 (1966).
109 Miller D.G. ibid. 71 616 (1967).
110 Miller D.G.,Pikal M.J. ibid. 74 1337 (1970).
111 Miller D.G.,Pikal M.J. J.Solution Chem. 1 111 (1972).
112 Mills R.,Kennedy J.W. J.Amer.Chem.Soc. 75 5696 (1953).
113 Mills R.,Adamson A.W. ibid. 77 3454 (1955).
114 Mills R. ibid. 77 6116 (1955).
115 Mills R. Nature 179 187 (1957).
116 Mills R.,Godbole E.W. Aust.J.Chem. 11 1 (1958).
117 Mills R.,Godbole E.W. J.Amer.Chem.Soc. 82 2395 (1960).
118 Mills R. Rev.Pure and Appl.Chem. 11 78 (1961).
119 Mills R.,Woolf L.A. 'The Diaphragm Cell', Aust.Nat. Univ.Press, Canberra, Australia, 1968.
120 Mills R. Ber.Bunsenges.phys.chem. 75 195 (1971).
121 Mills R. J.Phys.Chem. 77 685 (1973).
122 Moore D.H.,Opperman K. Biochim.Biophys.Acta 22 136 (1956).
123 Mouquin H.,Cathcart W.H. J.Amer.Chem.Soc. 57 1791 (1935).
124 Mysels K.J.,McBain J.W. J.Coll.Sci. 3 45 (1948).
125 Neilsen J.M.,Adamson A.W.,Cobble J.W. J.Amer.Chem.Soc. 74 446 (1952).
126 Nelson F. J.Polym.Sci. 40 563 (1959).
127 Nernst W. Z.phys.Chem. 2 613 (1888).
128 Northrop J.H.,Anson M.L. J.Gen.Physiol. 12 543 (1929).
129 Olsztain M.,Turq P.,Chemla M. J.Chim.Phys. 67 217 (1970).
130 Onsager L. Phys.Rev. 37 405 (1931);38 2265 (1931).
131 Onsager L. J.Phys.Chem. 36 2689 (1932).
132 Onsager L. Ann N.Y.Acad.Sci. 46 241 (1947).
133 Onsager l.,Kim S.K. J.Phys.Chem. 61 215 (1957).
134 O'Reilly D.E.,Peterson E.M. J.Chem.Phys. 55 2155 (1971)
135 Orr W.J.,Butler J.A.V. J.Chem.Soc. 1273 (1935).
136 Partington J.R.,Hudson R.F.,Bagnall K.W. Nature 169 583 (1952).
137 Paterson R. 'Irreversible Thermodynamics As Applied to Biological Systems',Chapter 5 in 'Membrane Metabolism and Ion Transport',Vol.1,Ed. E.E.Bitter, John Wiley and Sons, N.Y., 1970.
138 Philpot J.St.L. Nature 141 283 (1938).

139 Philpot J.St.L.,Cook G.H. Research 1 234 (1947).
140 Pikal M.J.,Miller D.G. J.Phys.Chem. 74 1337 (1970).
141 Pikal M.J. ibid. 74 4165 (1970).
142 Pikal M.J. ibid. 75 3124 (1971).
143 Pikal M.J. ibid. 76 3038 (1972).
144 Prigogine I. 'Introduction to Irreversible Thermodynamics', 3rd. Edition, Interscience,N.Y., 1967.
145 Pruppacher H.R. J.Chem.Phys. 56 101 (1972).
146 Rabinowitsch A.J. Z.physik.Chem. 99 338 (1921).
147 Reilly J.,Ray W.N. 'Physico-Chemical Methods', Vol.2, Methuen and Co.Ltd.,London, 1948.
148 Reilly P.J.,Stokes R.H. Aust.J.Chem. 23 1397 (1970).
149 Reilly P.J.,Stokes R.H. ibid. 24 1361 (1970).
150 Riley H.L.,Gallafent V. J.Chem.Soc. 522 (1922).
151 Robinson R.A.,Stokes R.H. 'Electrolyte Solutions', revised 2nd. Edition,Butterworths,London, 1965.
152 reference 151 Chapter 10.
153 reference 151 p.261.
154 reference 151 p.91.
155 reference 151 p.463.
156 Robinson R.A.,Wilson J.M. Trans.Far.Soc. 36 738 (1940).
157 Rutledge G. Phys.Rev. 40 262 (1932).
158 van Rysselberghe P.J.,Grunnell S.W.,Carlson J.M. J.Amer.Chem.Soc. 59 336 (1937).
159 Sahay J.N. J.Sci.In.Res. 18B 235 (1959).
160 Samoilov O.Ya. 'The Structure of Aqueous Solutions of Electrolytes and of Hydrated Ions', IZD-VO AN SSSR, Moscow, 1957.
161 Simpson J.H.,Carr H.Y. Phys.Rev. 111 201 (1958).
162 von Stackelberg M. Z.Elektrochem. 57 338 (1953).
163 von Stackelberg M.,Pilgram M.,Toome V. Z.Elektrochem. 57 342 (1953).
164 Stejskal E.O.,Tanner J.E. J.Chem.Phys. 42 288 (1965).
165 Stokes R.H. J.Amer.Chem.Soc. 72 763 (1950).
166 Stokes R.H. ibid. 73 3527 (1951).
167 Stokes R.H. Aust.J.Sci. 19 35 (1957).
168 Stokes R.H.,Woolf L.A.,Mills R. J.Phys.Chem. 61 1634 (1957).

169 Strafelda F.,Stastny M. Coll.Czech.Chem.Commun. 32 1836 (1967).

170 Svensson H. Acta chem.Scand. 5 72 (1951).

171 Thomas H.C. Proc.Natl.Acad.Sci.U.S. 42 909 (1956).

172 Trappeniers N.J.,Gerritsma C.J.,Oosting P.H. Phys.Lett. 18 256 (1965).

173 Turq P.,Lanteline F.,Roumegous Y.,Chemla M. J.Chim.Phys. 68 527 (1971).

174 Valiev K.A.,Emel'yanov M.I. J.Struct.Chem. 5 625 (1964).

175 Vasil'ev V.P.,Grechina N.K. Russ.J.Inorg.Chem. 9 357 (1964).

176 Vogel A.I. 'Textbook of Quantitative Inorganic Analysis', Longmans, 3rd. Edition, 1961.

177 Wall F.T.,Grieger P.F.,Childers C.W. J.Amer.Chem.Soc. 74 3562 (1952).

178 Wang J.H. ibid. 73 510 (1951).

179 Wang J.H. ibid. 74 1182 (1952).

180 Wang J.H.,Miller S. ibid. 74 1612 (1952).

181 Wang J.H.,Robinson C.V,,Edelman I.S. J.Amer.Chem.Soc. 75 466 (1953).

182 Wang J.H. J.Phys.Chem. 58 686 (1954).

183 Wang J.H. ibid. 69 4412 (1965).

184 Washburn E.W. J.Amer.Chem.Soc. 38 2431 (1916).

185 Weiss A.,Nothnagel K.H. Ber.Bunsenges.phys.chem. 75 216 (1971).

186 Woolf L.A.,Miller D.G.,Gosting L.J. J.Amer.Chem.Soc. 84 317 (1962).